

Lecture Notes for Thermal Physics, Phys 358, University of Waterloo

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What's new?

2023-07-14:

- A request! If you have used these notes and found them useful, or have suggestions, please get in contact, jddmartin@uwaterloo.ca, even if it's just a note to say hello!

2023-05-03:

- added link to interview with Schroeder.

These notes are intended to complement the course textbook: Schroeder's *Introduction to Thermal Physics* (SITP).¹ I mostly use the same notation, but condense, reorder, and elaborate on the material in ways that make sense to me. I will be grateful for your comments and/or corrections. I update these notes frequently. For the most recent version, please see:

https://www.dropbox.com/s/1m7zgtaueb0a2cp/lecture_notes_generated.pdf?dl=0

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1 Introduction

Thermal physics is the study of systems and processes where the concept of *temperature* is relevant.

In everyday life we don't generally require a precise definition of temperature. A reproducible measurement of *hotter and colder* is normally all that we need; e.g., is tomorrow expected to be warmer or colder than today? We only need to *order* and we can do so based on the criteria that heat flows from "hot to cold".

However, the precise definition of the temperature T of a system is straightforward enough, given its *energy* U and *entropy* S :

$$T := \left(\frac{\partial U}{\partial S} \right)_{\text{no work}} . \quad (1)$$

Of course we will need to define entropy and the "no work" constraint, but ultimately the precise definition of temperature is not problematic — the challenge is to understand *why* this definition is useful and how it relates to our everyday notion of temperature.

We shall start by following history's lead: In Part I of these notes we will define temperature empirically and gain familiarity with its use on the *macroscopic* level; i.e., mainly without using any knowledge of the atomic nature of matter. Such an approach is useful but limited. Nonetheless, Part I will provide a physical context for the discussion of the precise definition of temperature (Eq. 1) in Part II.

Also in Part I we will clarify the difference between the two mechanisms by which energy can flow into or out of a system: *heat* and *work*, establishing what the "no work" constraint means in Eq. 1.

In Part II we will introduce *entropy* S by examining the details of three specific "toy" systems at the microscopic (atomic) level. Although these *are* reasonable models of certain physical systems, they are chosen because they illuminate the general theory.² More specifically, these systems will motivate the precise definition of temperature given by Eq. 1 and the related *2nd law of thermodynamics*.

In Part III we will return to the macroscopic level of Part I, examining the implications of the precise definitions of temperature, entropy, and the 2nd law. For example, we will learn that there is an upper bound on the efficiency of internal combustion engines (which currently power most automobiles) given by the temperatures involved in their operation.

Finally, in Part IV, *Thermal radiation and the temperature of the earth*, we will apply the principles of thermal physics, as developed in Parts I to III, to an important problem. Although much of the material in this last part is covered by SITP, the treatment of these notes differs significantly — highlighting the relationship between thermal radiation and the historical development of quantum mechanics. This final Part IV is optional; i.e., UW Phys 358 students are not responsible for this material. However, it provides a nice "capstone", tying together many concepts from the course.

In the preface to his [Theory of Heat](#), Maxwell explains that "*In order to bring the treatment of these subjects within the limits of this textbook, it has been found necessary to omit everything which is not an essential part of the intellectual process by which the doctrines of heat have been developed,*

²Here I must emphasize that we are following the inspired approach of SITP.

or which does not materially assist the student in forming their own judgment on these doctrines.
What a wonderful sentiment! I wish you success in forming your *own* judgment.

2 Course plan

Assuming two lectures a week, each of 80 minutes, a standard term at UW consists of 22 lecture periods. The following is an approximate lecture plan — leaving two lecture periods free for midterms — with links to the corresponding sections of the notes.

2.1 Lecture topics

- L1
 - [1. Introduction](#)
 - Start Part I: Macroscopic phenomenological thermal physics
 - [B. Galilean thermometers and buoyancy](#)
 - [4.1. Liquid-in-glass thermometers](#)
 - Course logistics
- L2
 - [4.2. Constant volume gas thermometers](#)
 - [4.3. The absolute zero of temperature and the ideal gas law](#)
 - [5. The relationship between temperature and energy for an ideal gas](#)
- L3
 - [6. Constant pressure heat capacities and the 1st law of thermodynamics](#)
 - [7. Intensive and extensive thermodynamic variables](#)
- L4
 - [8. Expansion and compression work](#)
- L5
 - [9. Introduction to phase transitions](#)
- L6
 - [10. Enthalpy](#)
- L7
 - [11. Thermal conductivity](#)
- L8
 - Start Part II, Entropy and temperature
 - [12. Introduction](#)

- 13. The Einstein solid model
-

- L9
 - E. Stirling's approximation
 - 13.3. Large system limit

- L10
 - 13.4. The definition of temperature for Einstein solids
 - 13.5. The heat capacity of the Einstein solid

- L11
 - 15.1. The entropy of monatomic ideal gases (Sackur-Tetrode equation)

- L12
 - 15.2. The general definition of temperature
 - 15.3. Another check of the Sackur-Tetrode equation

- L13
 - 16. The 2nd law of thermodynamics

- L14
 - 17. The 3rd law of thermodynamics?
 - 18. Microscopic closing words

- L15
 - Start Part III, Macroscopic thermal with entropy
 - 20. Cyclic heat engines

- L16
 - 22. Cyclic refrigerators

- L17
 - 23.1. Helmholtz free energy

- L18
 - 23.2. Gibbs free energy and the phase transitions of pure substances
 - 23.3. The Clausius-Clapeyron relation

- L19
 - 24. The available work interpretation of Helmholtz and Gibbs free energies

- L20
- 25.1. Thermodynamic identities
 - 25.2. Maxwell's relations
 - 25.3. The general relationship between the constant pressure and constant volume heat capacities
-

3 Some abbreviations, symbols, and housekeeping matters

symbol	meaning
SITP	Schroeder's <i>Introduction to thermal physics</i>
JDDM	yours truly
UW	University of Waterloo
\equiv	definition (e.g. $C_V \equiv (\partial U / \partial T)_V$); I'm gradually abandoning \equiv in favour of the more logical, asymmetric equivalents:
\coloneqq	definition (symbol on LHS is being defined)
\coloneq	definition (symbol on RHS is being defined)
$\overset{?}{=}$	an incorrect or dubious result
//	end of proof or demonstration (when handwritten)
\square	end of proof or demonstration
OED	Oxford English Dictionary http://oed.com (freely available through on-campus network)
op. cit.	in the work previously mentioned or quoted (source: OED)
cf.	compare (source: OED)
XX	placeholder for material to be corrected or added later
	link to a video that I have made (Microsoft Streams version, no ads, UW only)
	link to a video that I have made (Youtube version)

New terminology is introduced in these notes using **bold-face**.

I have extensively hyperlinked to both external resources and locations *within* this document. For some reason, the “back button” action is not always obvious in pdf readers, but normally [is available](#).³ (Unfortunately the Dropbox pdf viewer does not have a back button.)

Earlier sections are accompanied by a video “mini-lecture” e.g., You *might* find it useful to watch these videos before reading the corresponding section. However, these videos do not contain any more information than the notes, and since I occasionally misspeak and am generally not as thorough as in the notes, some students might find it more efficient not to watch them at all and just stick to the notes. Making videos is new to me, so I will be grateful for your feedback.

There are also small number of additional links to video demos and documentaries that are mostly just for entertainment. You can ignore these links, unless indicated otherwise. I've wasted hours on youtube, so that you don't have to. Don't let my efforts be in vain!

I have boxed what I think are the important equations; but I consider it beneficial for you to make that sort of decision for yourself — possibly creating personalized formula sheet for your own future reference.

These notes contain references to journal articles. Some are to acknowledge the sources that I have used and may not be particularly useful to look at — I've tried to explicitly indicate which ones might be useful. These references will also normally be links that take you directly to the “official” journal page for the articles. These pages will offer the option to purchase the article; however, if

³I use the Atril pdf viewer on Linux. In version 1.20.1, “Edit → Toolbar” allows you to drag a “← Back” icon onto your toolbar.

you are a UW student **it is not necessary to pay for these articles**, as both these articles and SITP may be freely accessed using the library: <https://login.proxy.lib.uwaterloo.ca/login>
(Please contact me if you have problems accessing an article freely.)

Part I

Macroscopic phenomenological thermal physics

Specialization is for insects.

Robert Heinlein, *Time enough for love*

4 Temperature measurement

4.1 Liquid-in-glass thermometers (SITP 1.1)⁴

- in Part II of these notes, we will motivate and define **temperature** precisely. Here we start with a pragmatic alternative: define temperature empirically using a Hg (mercury) thermometer.

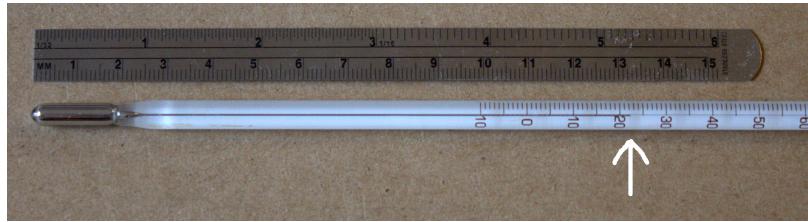


Figure 1: A Hg thermometer from my laboratory. The arrow marks location of the observed liquid-vapour boundary at $\approx 22^\circ\text{C}$. Even this simple thermometer can be used to study interesting phenomena .

Source: JDDM

- as the liquid Hg expands with increasing temperature, the liquid-vapour ($\ell\text{-}v$) boundary extends further down the tube.
- how do we put the **scale** on the thermometer? i.e., the numbers and marks that give the correspondence between the location of the $\ell\text{-}v$ boundary and temperature. For this purpose, note that whatever the “correct” definition of temperature, in our everyday experiences:
 - if two isolated objects are put into contact for a sufficient amount of time, they tend to reach the same temperature (so-called **thermal equilibrium**).
- this observation suggests a procedure for adding the scale.⁵
 - put the thermometer in contact with an ice-water slush bath, wait for thermal equilibrium, and then mark off the location of the $\ell\text{-}v$ boundary as 0°C .
 - put the thermometer in contact with boiling water, wait for thermal equilibrium, and then mark off the location of the $\ell\text{-}v$ boundary as 100°C .

⁴Annotations in the section titles, such as “SITP 1.1”, indicate the corresponding sections of the text: D. V. Schroeder, *An introduction to thermal physics* (Addison Wesley, San Francisco, CA, 2000).

⁵The water should be at normal atmospheric pressure — we will discuss later in the course how the boiling point depends on pressure. The freezing point is less sensitive to pressure.

3. mark off locations between (and beyond) the two **fixed points** of 0 and 100 °C using linear interpolation (and extrapolation). i.e., set the scale of the thermometer.

The location of the ℓ - v boundary on the scale now indicates the temperature of the thermometer on the Celsius scale.⁶

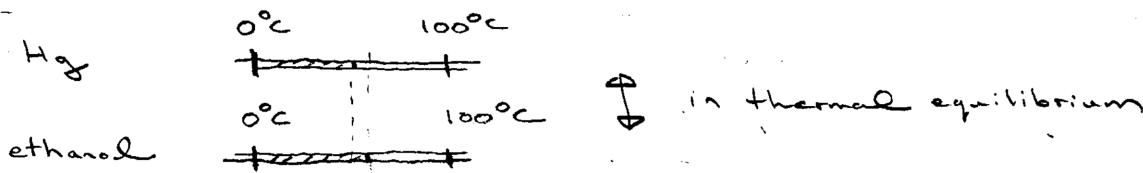
- instead of Hg (which is toxic), simple inexpensive thermometers often use alcohols — dyed red for visibility, e.g., from Canadian tire. The generic term for both Hg and alcohol thermometers is **liquid-in-glass thermometers**.

Example: SITP Problem 1.7

- since the procedure for adding a scale didn't seem to rely on any special property of Hg, an important question immediately comes to mind:

Does the temperature scale defined by our procedure depend on the specific liquid used?

- yes (unfortunately); the type of liquid *does* matter. Construct two thermometers and calibrate them both by the same procedure. By construction they automatically agree at 0 °C and 100 °C. However, experiment shows that they do not agree at intermediate temperatures:



- here is a quantitative comparison between three thermometers using different liquids. The thermometers are placed in a water bath that is heated from freezing to boiling. The three “temperatures” — as read by the thermometers — are noted at various intermediate points:⁷

mercury “alcohol” water

0 °C	0 °C	0 °C	← automatic agreement
25 °C	22 °C	5 °C	
50 °C	44 °C	26 °C	
75 °C	70 °C	57 °C	
100 °C	100 °C	100 °C	← automatic agreement

from H. Chang, “Spirit, air, and quicksilver: The search for the “real” scale of temperature”, [Historical Studies in the Physical and Biological Sciences 31, 249–284 \(2001\)](#)

- given the disagreement between the thermometers, is there any way to decide which one is more correct? If we knew, we could use it to **calibrate** the other thermometers. But how do we define “correct”?

⁶An entertaining account of Celsius’ contribution to “his” scale is given by: <https://youtu.be/rjht4oAByCI>, including a discussion of the more refined modern definition.

⁷The term “alcohol” is a bit vague, referring to so-called “spirit of wine” — an archaic term for distilled wine, which would mostly consist of ethanol together with some water. The table shows historical data; the precise composition of the “alcohol” is unknown.

- even if we could figure out which liquid (if any) was the “one true thermometer”, it would still only work over a limited temperature range; e.g., Hg freezes at $\approx -40^\circ\text{C}$.
- we *need* to define temperature in a way that does not depend on the properties of any specific material. We will do so partially in the next section, further developing our empirical, operational approach. However, it is also desirable that our definition of temperature provide some theoretical basis for the observation that “heat flows from hot to cold”. For this we will need to wait for the formal definition in Part II.
- there are many different types of empirical thermometers, similar to the liquid-in-glass thermometer. Appendix B discusses the Galilean thermometer, which relies on the temperature variation of buoyancy in a liquid. It is useful to study its principles of operation as many applications of thermal physics involve buoyancy.

Suggested problem: SITP Problem 1.7

4.2 Constant volume gas thermometers (SITP 1.1, 1.2)

- we now consider using the properties of gases — instead of liquids — to measure temperature. Suppose that a gas is contained within a constant volume. We expect that its pressure depends on temperature; i.e., pressure increases with temperature. We want to use this relationship in reverse — use easily measured pressures to deduce temperature. The hope is that such a **constant volume gas thermometer** is more universal than the liquid-in-glass thermometers; i.e., it does not depend on what type of gas we use.
- to be specific, I will discuss thermometers constructed and tested by Regnault.⁸ His measurements are remarkably accurate, given the technology available at the time (≈ 1850).
- Regnault was able to “fill” his constant volume gas thermometers with air at atmospheric pressure but different temperatures. Once they were filled they were sealed, and it was possible to measure the pressure required to keep them at constant volume. Since the technology of pressure measurement has vastly improved since that time, we will not discuss the specifics of how he measured pressures (see, for example, Fig. 1-7 of M. W. Zemansky, *Heat and thermodynamics; an intermediate textbook*, 5th edition (McGraw-Hill, New York, 1968)).
- Regnault created two constant volume gas thermometers:
 - one was filled with air at atmospheric pressure and at a temperature of 0°C (as determined by the melting of ice).
 - the other was filled with air at atmospheric pressure and at a temperature of 100°C (as determined by the boiling of water).
- if thermometer 1 is raised to the boiling point of water, its pressure rises above atmospheric pressure. Likewise, if thermometer 2 is lowered in temperature to the melting point of ice, the measured pressure drops below atmospheric pressure:

⁸In discussing Regnault’s work I am relying on the (excellent) secondary source: H. Chang, *Inventing temperature: measurement and scientific progress*, Oxford Studies in Philosophy of Science (Oxford University Press, Oxford ; New York, 2007).

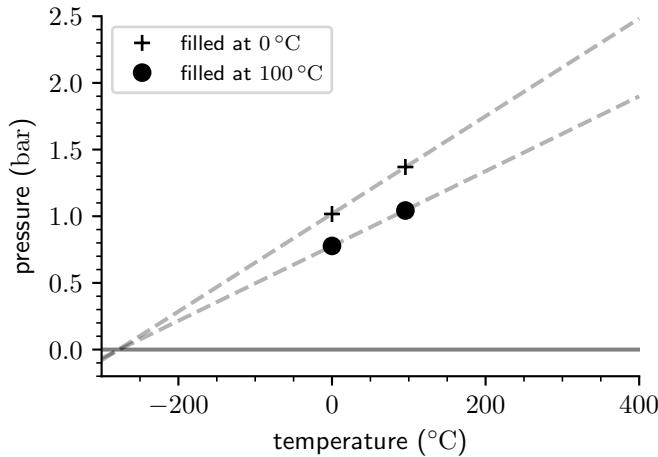


Figure 2: Measurements of pressure for two constant volume gas thermometers. The fitted dashed lines “set the scale” i.e., the assumed relationship between measured pressure and temperature that enables pressure to serve as a proxy for temperature. The data is from Table 2.5 of H. Chang, *Inventing temperature: measurement and scientific progress*, Oxford Studies in Philosophy of Science (Oxford University Press, Oxford ; New York, 2007).

- as with the Hg thermometer we use linear interpolation and extrapolation to “set the scale” (the dashed lines of Fig. 2).
- for each thermometer we now have a (hypothesized) pressure-temperature relationship that allows measured pressures to determine temperature. But how do we know this relationship is correct? Trick question (!) — we can not answer it without a formal definition of temperature. Instead, as in the case of the liquid-in-glass thermometers, we merely look for *consistency*.
- Regnault used the two thermometers to simultaneously measure the temperature of an oil bath, and examined the differences in temperatures indicated by each thermometer:

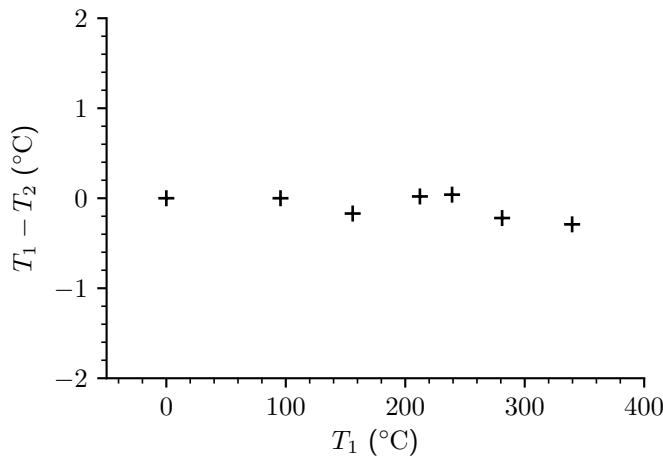


Figure 3: Comparison between the temperature readings of two different constant volume gas thermometers. Each of the thermometers uses a gas of different density. Note that agreement is automatic at the two fixed points 0°C and 100°C that we used to “set the scales” (like for liquid-in-glass thermometers). The data is from Table 2.5 of H. Chang, *Inventing temperature: measurement and scientific progress*, Oxford Studies in Philosophy of Science (Oxford University Press, Oxford ; New York, 2007).

- Figure 3 shows good agreement, the dominant deviations apparently due to “random” errors, rather than indicating systematic differences.⁹
- Regnault also compared air thermometers to both H_2 and CO_2 based gas thermometers using a similar procedure, and found good agreement. (However, agreement with sulphuric acid vapour was quite poor, presumably related to the ease at which this vapour can be partially liquified.)
- it certainly seems that the constant volume gas thermometer has a “universal” aspect, not related to the specifics of the density or type of gas (within limitations).

4.3 The absolute zero of temperature and the ideal gas law 🎥 🎥 (SITP 1.1, 1.2)

- examine the extrapolated temperature pressure relationships for both thermometers given in Fig. 2. Note that they both indicate that zero pressure would be obtained if we could lower the temperature to $\approx -270^\circ\text{C}$.
- based simply on the observation of the common extrapolation point of -273°C , without any theoretical considerations (yet), it makes sense to set the “zero” of our temperature scale at this temperature — **absolute zero** — instead of the freezing point of water. Doing so but maintaining the difference between water freezing and boiling at 100 units, roughly speaking, is the **Kelvin (K) temperature scale**. The freezing point of water is $\approx 273\text{ K}$ whereas its boiling point is $\approx 373\text{ K}$.

⁹To rigorously compare the thermometers, we would have to determine that these small differences were within “experimental error”.

- although we have concentrated on the constant volume gas thermometer, it is also possible to construct **constant pressure gas thermometers**, in which a fixed amount of gas is held at a constant pressure and its *volume* is used as a proxy for temperature (in agreement with temperatures measured using constant volume gas thermometers).
- all of these results are just special cases of the first great “unification” of physics, the **ideal gas law**. Specifically, all *low density* gases, regardless of their composition, behave in a generic fashion, of which you are undoubtedly aware:

$$PV = NkT \quad (2)$$

where N is the number of molecules¹⁰ in the volume V , exerting pressure P , and Boltzmann’s constant: $k \approx 1.38 \times 10^{-23} \text{ J/K}$. Alternately, if we express the number of molecules in terms of the **Avogadro constant** $N_A \approx 6.022 \times 10^{23} \text{ mol}^{-1}$, as $N = N_A n$, we have

$$PV = nRT \quad (3)$$

where $R := N_A k$ and n is the the number of **moles** (corresponding to the unit **mol** in expressions). Incidentally, since N (or n) only refers to the number of molecules, independent of their type, our statement of the ideal gas law implies [Dalton’s law of partial pressures](#).

- both forms of the ideal gas law, Eq.’s 2 and 3, are equivalent if n and N are chosen to correspond to the same amount of gas i.e., $n = N/N_A$. Sometimes it is more convenient to use the nR version when computing “macroscopic” quantities, as large numbers may be avoided e.g., the number of molecules. However, when considering things from the more fundamental molecular level, as in Section 5, and Part II, the Nk version is normally used.
- the ideal gas law is our first example of an **equation of state**: a relationship between P , V and T for a given amount of material. Normally they will not be quite as simple as the ideal gas law. Nonetheless the fact that an underlying equation of state merely exists — even if its explicit form is not known — is often a crucial part of thermodynamic arguments.
- we can not decide how accurate the ideal gas law is if we do not have a precise definition of temperature. However, we can turn this situation around and *use the ideal gas law to define temperature* (temporarily). i.e., in the limit of sufficiently low enough density, we may define the temperature of a gas to be:

$$T := \frac{PV}{nR} \quad \text{an operational definition,} \quad (4)$$

and *for now* accept as an empirical fact that when temperatures as defined this way, the “heat flows from hot to cold” behaviour is observed.

- we may calibrate so-called **secondary thermometers**, such as the liquid-in-glass thermometers, by putting them in thermal contact with gas thermometers. These secondary thermometers will typically be more practical to use.¹¹

¹⁰Here and elsewhere a molecule could be an actual molecule e.g., O_2 , N_2 , H_2O , but could also be an atom e.g., He, Ar. This ambiguous usage is common and whether or not “molecule” actually refers to an entity of more than one atom is normally clear based on the context.

¹¹Although defining temperature using ideal gases is a bit lame (a deficiency that we shall correct in Part II), gas thermometers are quite useful for the implementation of primary temperature standards. For details see: M. W. Zemansky, *Heat and thermodynamics; an intermediate textbook*, 5th edition (McGraw-Hill, New York, 1968).

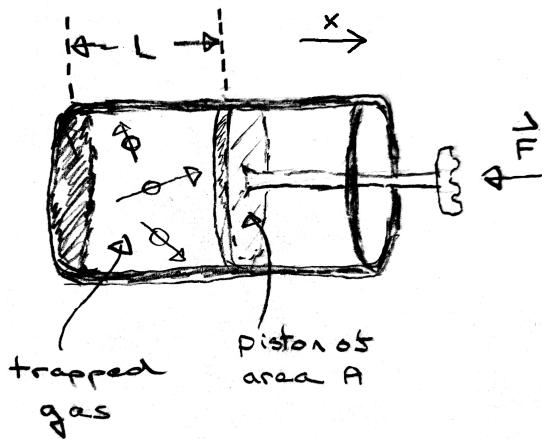
5 The relationship between temperature and energy for an ideal gas

- after we give the exact definition of temperature in Part II, we will actually be able to “derive” the ideal gas law (under certain assumptions), showing a certain internal consistency to our approach.

5 The relationship between temperature and energy for an ideal gas (SITP 1.2, 1.3)

-

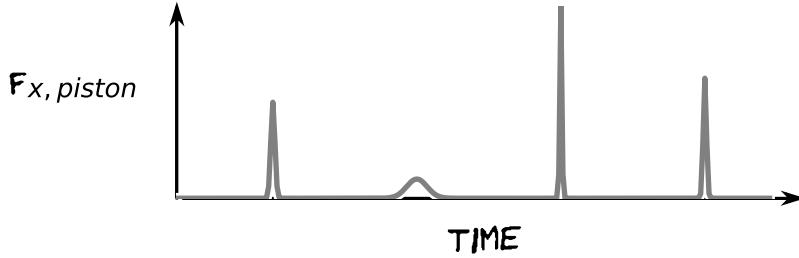
- when two objects in contact eventually reach the same temperature (thermal equilibrium) we might suspect that this is accomplished through the transfer of **energy** between them, suggesting that there is a relationship between the temperature of a body and the energy that it contains.
- we anticipate that the specific relationship between the temperature and energy of a body will depend on — among other things — its size and composition. We will certainly need to have a proper definition of temperature to determine this relationship for an arbitrary body.
- however we already have a definition of temperature for an ideal gas (Eq. 4), so we will start by attempting to derive the relationship between temperature and energy for ideal gases.
- consider a cylinder with a movable **piston**:



We imagine the idealized situation that the piston-wall contact is frictionless and that the piston must be held in place against the pressure of the gas by pushing leftwards on the handle.

- if a gas is contained within the cylinder, the pressure on the piston is due to the forces exerted by the collisions of gas molecules with the piston surface. Recall that pressure is the force per unit area.
- to start, consider just a single gas molecule within the cylinder. What force will this single molecule exert on the piston? Most of the time: *none*. Only when the molecule collides with the piston is any force exerted on the piston.¹²

¹²Normally, where it is both possible and beneficial, I will show real data in plots. In cases where a plot is just intended to show a trend, idea or definition and not be quantitative — such as here — I will use “xkcd” styling (in progress).



- let us refine our question, asking instead: what is the *average* force on the piston due to the molecule?
- the time average \bar{A} of any quantity A may be defined as:¹³

$$\bar{A} := \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A(t). \quad (5)$$

Thus, if we know the area under each “bump” and the time between them, we will be able to compute the average force that the molecule exerts on the piston.

- the area under each spike is constant, independent of exact acceleration profile for each molecule. To see this, consider the force on the molecule during a collision:

$$F_{x,\text{molecule}}(t) = ma_x(t) \quad (6)$$

and integrate over the time interval of a single collision:

$$\int_{\text{collision}} F_{x,\text{molecule}}(t) dt = m \int_{\text{collision}} a_x(t) dt \quad (7)$$

$$= m\Delta v_x. \quad (8)$$

Thus the time integral of the force acting on the molecule over the duration of the collision — the **impulse** — has to be the total change in the molecule’s x momentum due to the collision. If we assume completely elastic, **specular**¹⁴ collisions with the wall, $\Delta v_x = -2v_x$, $\Delta v_y = 0$ and $\Delta v_z = 0$, and thus the impulse is:

$$\int_{\text{collision}} F_{x,\text{molecule}}(t) dt = -2mv_x. \quad (9)$$

Remembering Newton’s 3rd law (equal and opposite forces), the impulse that the *piston* receives due to the collision will be:

$$\int_{\text{collision}} F_{x,\text{piston}}(t) dt = - \int_{\text{collision}} F_{x,\text{molecule}}(t) dt \quad (10)$$

$$= 2mv_x. \quad (11)$$

¹³You may think of this definition for \bar{A} as a continuous generalization of the more familiar average of a discrete set of N quantities:

$$\bar{A} := \frac{1}{N} \sum_{i=1,N} A_i.$$

¹⁴Here **specular** means “like rays of light reflecting from a mirror surface”.

5 The relationship between temperature and energy for an ideal gas

This impulse corresponds to the area under each one of the bumps in the plot of $F_{x,\text{piston}}$ versus time. If v_x before each collision is the same, the impulses will be the same.

- the time averaged force can be computed using the recipe of Eq. 5 since we now know the impulse for each collision. We just need the time interval between the collisions Δt . For the simple geometry of Fig. 1.4 of SITP:

$$\Delta t = 2L/v_x. \quad (12)$$

Combining with the impulse of Eq. 11 and time averaging using Eq. 5 gives:

$$\bar{F}_{x,\text{piston}} = \frac{1}{\left(\frac{2L}{v_x}\right)} 2mv_x \quad (13)$$

$$= \frac{mv_x^2}{L}. \quad (14)$$

The average pressure exerted on the piston due to the single molecule is thus:

$$\bar{P}_{\text{molecule}} = \frac{\bar{F}_{x,\text{piston}}}{A} \quad (15)$$

$$= \frac{mv_x^2}{LA} \quad (16)$$

$$= \frac{mv_x^2}{V}. \quad (17)$$

where V is the enclosed volume ($V = LA$ for the simple geometry of Fig. 1.4 of SITP).

- if instead of a single molecule inside the piston, we add the pressures due to N molecules (all of the same species) the total pressure is:

$$\bar{P} = N\bar{P}_{\text{molecule}} \quad (18)$$

$$= N \frac{m\langle v_x^2 \rangle}{V}, \quad (19)$$

where we have allowed for the possibility that the different molecules have different velocities by introducing $\langle \dots \rangle$ to denote an average over *all molecules*.

- as far as the gas is concerned, there is nothing special about the x -direction, and thus we expect that $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$, so that Eq. 19 can be written as:

$$\bar{P} = \frac{N}{V} m \frac{(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle)}{3}. \quad (20)$$

- it is a general property of averages that *the sum of averages is the same as the average of*

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sums. In this case: $\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle$, so we can rewrite Eq. 20 as:

$$\bar{P} = \frac{N}{3V} 2 \underbrace{\frac{1}{2}m (\langle v_x^2 + v_y^2 + v_z^2 \rangle)}_{\text{average kinetic energy per molecule} := \langle KE_{\text{molecule}} \rangle} \quad (21)$$

$$= \frac{2N}{3V} \langle KE_{\text{molecule}} \rangle. \quad (23)$$

- recall that we are working with an ideal gas, so that:

$$P = \frac{NkT}{V} \quad (24)$$

If both Eq.'s 23 and 24 are to be true, we can equate them and rearrange to give:

$$\langle KE_{\text{molecule}} \rangle = \frac{3}{2}kT. \quad (25)$$

- thus if the *only* way that the ideal gas can store energy is through the kinetic energy of its molecules, the total energy U of an ideal gas of N molecules is:

$$U = N \frac{3}{2}kT. \quad (26)$$

- we made some assumptions in deriving this relationship between the energy of an ideal gas U and its temperature T :
 - our geometry was relatively simple ($V = LA$),
 - collisions with the walls are specular and the molecule loses no energy in colliding with the wall, and
 - all of the energy of the gas is due to the kinetic energy of its molecules.

For these reasons, we should check whether or not Eq. 26 actually agrees with experiment.

-
- consider an experimental setup to test Eq. 26. A resistor heats a gas contained within a fixed volume:

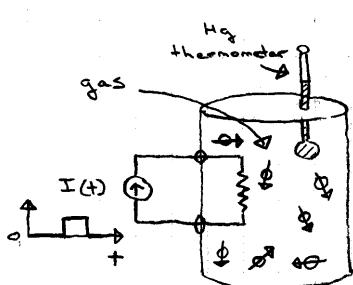


Figure 4: Measurement of the relationship between U and T for a gas. A current pulse of magnitude I_0 and duration Δt , deposits energy $\Delta U = RI_0^2\Delta t$ into the resistor (so-called **Joule heating**¹⁵). Some fraction of this energy will be transferred to the surrounding gas and the resulting increase in its temperature measured. In practice this experiment would be difficult to make quantitative — we will discuss more practical techniques later. Nonetheless, it is a useful thought experiment.

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- in the limit of small ΔU and ΔT , we may characterize our results using the **heat capacity at constant volume**:¹⁶

$$C_V := \left(\frac{\partial U}{\partial T} \right)_V \quad (27)$$

for which Eq. 26 predicts:

$$C_V = N \frac{3}{2} k. \quad (28)$$

- the physical properties of various gases, including heat capacities, are available at <http://webbook.nist.gov/chemistry/fluid/>.¹⁷ I have downloaded the heat capacity C_V data for all gases in the database. Expressing them in the dimensionless form $C_V/(Nk)$ accounts for the experimental observation that the heat capacity is proportional to the amount of the substance:

¹⁵For a short interesting account of the scientific work of Joule, see the video:

<https://archive.org/details/JamesPrescottJouleWilliamThomsonAndTheDiscoveryOfEnergy>

¹⁶The “subscripted” V in $(\frac{\partial U}{\partial T})_V$ means that while taking the derivative of U wrt T , we should hold V constant. We use this subscript notation when there is the possibility that a quantity we are differentiating could be expressed as a function of different variables. For example, here we are considering U to be a function T and V . But since there is an underlying equation of state (e.g., the ideal gas law) that tells us P given T and V , we could instead write U as a function of T and P . That would allow us to evaluate $(\frac{\partial U}{\partial T})_P$ instead of $(\frac{\partial U}{\partial T})_V$. These derivatives are not necessarily equal. (Although — as we see shortly in Section 6 — they do turn out to be equal for the special case of an ideal gas.) For more information, see the discussion of “derivatives under a change of coordinates” in Appendix A.

¹⁷This is a web-site of the U.S. Department of Commerce’s National Institute of Standards and Technology (NIST), an authoritative source of physical data, including the most recent values of the [fundamental constants](#).

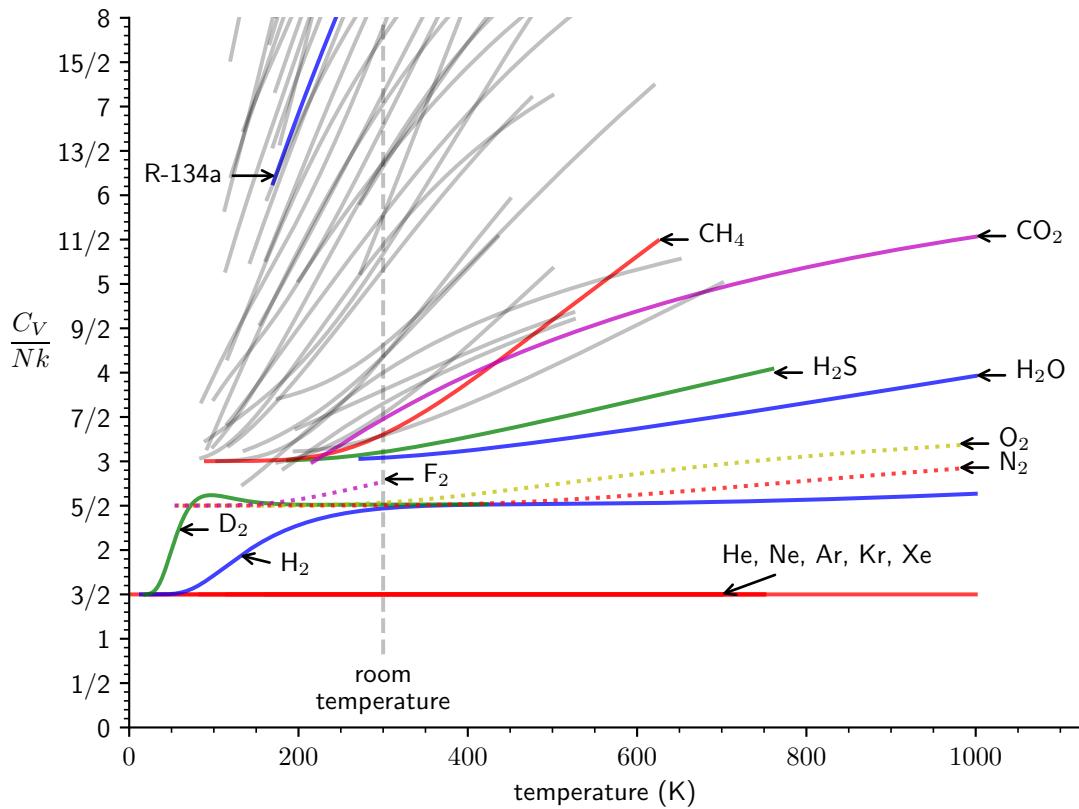


Figure 5: The C_V 's of various gases, in the limit of low densities, as obtained from the database: <http://webbook.nist.gov/chemistry/fluid/>. All monatomic and diatomic species are labelled. All unlabelled curves correspond to triatomic or larger species. The larger molecules are in the database as they are used in common applications such as refrigeration. For example, the **R-134a** label on the plot refers to 1,1,1,2-tetrafluoroethane (CH_2FCF_3), commonly used in automobile air-conditioners. To give an objective view of the validity of equipartition theorem, all molecules in the database with $C_V/(\frac{1}{2}Nk)$'s < 16 are shown; except for clarity I have omitted carbon monoxide, deuterium oxide, and parahydrogen. (Parahydrogen is a special state of H_2 for which a discussion would be distracting at this point; see Problem 6.30 of SITP.)

- Figure 5 illustrates that:
 - 1) The C_V 's of noble gases ($\text{He}, \text{Ne}, \dots$) are consistent with Eq. 28.
 - 2) Except for H_2 and D_2 at low temperatures ($\lesssim 50$ K), the C_V 's for molecules are higher than those predicted by Eq. 28.
 - 3) The diatomic gases show a propensity towards $C_V/N = \frac{5}{2}k$. Some of the triatomic gases ($\text{H}_2\text{O}, \text{H}_2\text{S}, \text{CH}_4$) show a propensity towards $C_V/N = 3k$ at low temperatures. On the other hand CO_2 and the heavier molecules (R-134a and all the grey lines) don't show a

propensity towards any special values of C_V .

These higher C_V 's are due to the internal motions of the molecules i.e. not all of the energy is stored in the kinetic energy of the molecules — they can store additional energy by rotating and vibrating, that is not accounted for in Eq. 28.

- the observed C_V/N 's, and the seemingly special values of $\frac{3}{2}k$, $\frac{5}{2}k$, $3k$ (all integer multiples of $\frac{1}{2}k$) can be partially rationalized using the **equipartition theorem**, which gives the internal energy of a gas of N molecules as:

$$U = f \frac{1}{2} N k T \quad (29)$$

where f is the number of **degrees of freedom** per molecule that contribute quadratic-like terms to the energy. Specifically, $f = 3$ if the only means of energy storage is translational. For diatomic molecules such as N_2 and O_2 near room temperature, $f = 5$, since they can also rotate in addition to moving.

- since dry air is 78% N_2 and 21% O_2 by volume, it is a reasonable approximation to assume that for air at room temperature $f = 5$, corresponding to $C_V = \frac{5}{2}Nk$ (an assumption you can make use of on your problem sets and exams unless otherwise advised). You may also assume that $f = 3$ for a monatomic ideal gas as well, corresponding to $C_V = \frac{3}{2}Nk$.
- in these notes, I de-emphasize the equipartition theorem, in comparison to SITP. My reasons and some additional information are contained in Appendix C (optional).

6 Constant pressure heat capacities and the 1st law of thermodynamics (SITP 1.4, 1.6)

-
- I have shown how C_V might be measured for gases, at least in principle (Fig. 4). For solids and liquids, heat capacities are normally made under conditions of constant *pressure*, not volume. This is because it can take quite large changes in pressure to confine a solid or liquid within a constant volume as temperature changes. It is easier just to allow expansion under constant surrounding pressure as temperature changes. The quantity measured is the **heat capacity at constant pressure**, C_P (to be defined shortly):

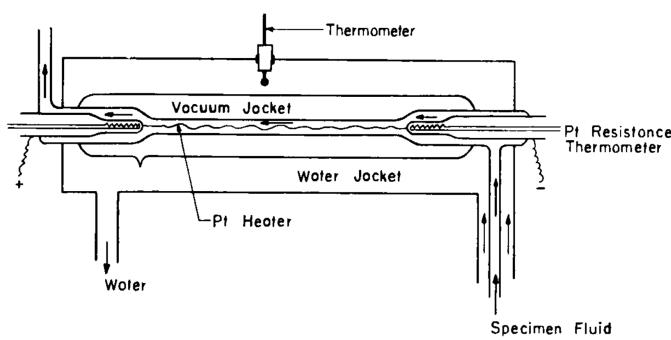


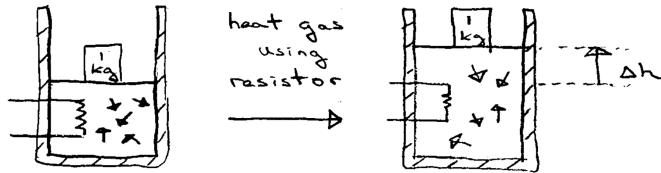
Figure 6: A steady flow electric calorimeter for measuring C_P of fluids (from Estermann (ed.), *Methods of Experimental Physics, Volume 1, Classical Methods*, page 270). The flow rate, electrical power input, and temperature difference between entering and exiting fluid allow C_P to be determined. An advantage of this particular arrangement is that the flow rate can be varied to estimate the systematic error due to heating the *container* of the fluid rather than the fluid itself.

- we might think that based on $C_V := (\frac{\partial U}{\partial T})_V$ that it makes sense to define:

$$C_P := \left(\frac{\partial U}{\partial T} \right)_P . \quad \text{wrong} \quad (30)$$

However, this is not the definition of C_P . To understand why:

- consider a piston-cylinder system set up so that 1) we can add heat to the gas within the cylinder using Joule heating, and 2) when the piston moves it can raise a weight in a constant gravitational field, thereby doing work:



- the force required to hold the weight is constant, so that the pressure of the gas within the cylinder is the same before and after the heating.
- the work done *on* the weight is:

$$W_{\text{on weight}} = F\Delta h \quad (31)$$

$$= PA\Delta h \quad (32)$$

writing $A\Delta h$ in terms of the change in the gas volume:

$$= P\Delta V \quad (33)$$

- note that

$$W_{\text{by a system}} = -W_{\text{on the system}} \quad (34)$$

- the mechanical work done *on* a system due to volume changes will be known as the **expansion/compression** work W_{mech} . In this case $W_{\text{mech}} = -P\Delta V$. Although we have considered a piston-cylinder geometry, this result is general: the expansion/compression work done on a system when its volume changes while at a certain pressure is always $-P\Delta V$, independent of the shape of the system before and after. All that matters is the change in volume. (However the qualifying “*while at a certain pressure*” is important.)
- since there are two ways that energy can enter or leave the gas system, we write:

$$\underbrace{\Delta U}_{\substack{\text{change} \\ \text{in internal} \\ \text{energy} \\ \text{of system}}} = \underbrace{Q}_{\substack{\text{heat} \\ \text{flow} \\ \text{into} \\ \text{system}}} + \underbrace{W_{\text{mech}}}_{\substack{\text{work} \\ \text{done} \\ \text{on} \\ \text{system}}} . \quad (35)$$

When a gas expands, it does work on its environment. In this case $W_{\text{mech}} < 0$ and so we have to heat the system more (Q is higher), to get the same ΔU , compared to the constant volume case where $\Delta U = Q$.

- there are other types of work besides expansion/compression work. For example, we will later consider that a battery can do electrical work. The generalization.¹⁸

$$\boxed{\Delta U = Q + W} \quad (37)$$

where W includes *all* types of work that can be done on a system (i.e. $W = W_{\text{mech}} + W_{\text{electrical}} + \dots$) is known as the **1st law of thermodynamics**. As the course proceeds it will become more clear how we separate the heat flow Q from the many ways that work W can be performed on a system.

- a heated gas held at constant pressure will expand, doing work. Thus its change in energy ΔU does not just correspond to the heat added Q . Consequently, instead of using Eq. 30, we will define the heat capacity at constant pressure to be:¹⁹

$$C_P := \lim_{\Delta T \rightarrow 0} \frac{Q}{\Delta T} \Big|_{\text{constant } P}. \quad (38)$$

If the system is *only* allowed to do expansion/compression work, so that:

$$Q = \Delta U - W \quad (39)$$

$$= \Delta U + P\Delta V \quad (40)$$

then

$$C_P = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta U + P\Delta V}{\Delta T} \right) \Big|_{\text{constant } P} \quad (41)$$

$$\boxed{C_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P}. \quad (42)$$

This expression applies to any system (not just ideal gases). However it simplifies greatly in the special case of ideal gases.

- 

¹⁸There is an alternate convention to be aware of (e.g. Fermi's *Thermodynamics* and also Section's 4.1 and 4.3 of SITP), in which we write

$$\Delta U = Q - W \quad \text{alternate convention} \quad (36)$$

where W is the work done *by* the system. This convention is employed because a frequent application of the basic laws of thermodynamics is heat engines, for which $Q > 0$ (the system takes heat from its surroundings) and *does* work on its surroundings. In this case, with the convention of Eq. 36, $W > 0$, which is a bit more convenient i.e., not having to carry around a negative sign.

¹⁹The notation here is somewhat imprecise and suggests an incorrect interpretation of Q . More specifically we should not view Q as a function of P and T ; it is not a "fluid" that flows between materials (the outdated caloric theory). **Some say:** *heat is not a noun*, but that's a bit too rigid. The important point is that Q is specific to processes — how we make changes — not solely the initial and final conditions. Later we will give a better definition of C_P (Eq. 93).

- rearranging $PV = NkT$:

$$V = \frac{NkT}{P} \quad (43)$$

and thus

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{Nk}{P} \quad (44)$$

So, for an ideal gas, Eq. 42 simplifies to:

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + Nk \quad (45)$$

What about the first term in the case of an ideal gas?

- consider an experiment done by Joule. Two gas cylinders connected by a valve are placed in a water bath and the temperature of the bath is monitored:

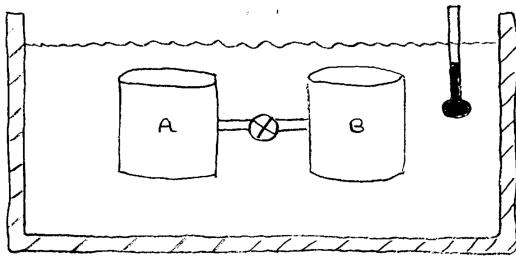


Figure 7: A schematic representation of Joule's set up for measuring temperature changes associated with the free expansion of a gas. The cylinders are immersed in a water bath within an insulated container.

- initially the valve \otimes is closed; A is filled with gas and B is evacuated. The gas in A is at the same temperature as the surrounding water bath.
- the valve \otimes is opened, gas flows from A to B until equilibrium is established (uniform density and pressure throughout the two cylinders). No work is done by the gas in this step.²⁰
- observations of the thermometer show no discernible change in the temperature of the water bath.

These results are consistent with both²¹

$$\Delta U = 0 \text{ and } \Delta T = 0$$

for the gas, despite the fact that it has undergone a change in its volume and pressure.

- this observation supports the conjecture:

The average energy U per molecule of an ideal gas can be written in a form depending *only* on the temperature and type of molecules.

²⁰Note that $\Delta V \neq 0$ — evidently it is not always true that for all processes $W_{\text{mech}} = -P\Delta V$. We will return to this point shortly.

²¹Joule's experiment is a **null experiment**: it sets an upper bound on the magnitude of ΔU (more precisely a *statistical* upper bound). An experiment can not *prove* that a quantity is exactly zero.

If true, we can write U/N as a function of T alone (using a different function for each molecular species). For now I ask you to accept this conjecture as an empirically supported fact,²² but later in the course — after we have developed the machinery to do so — we will show that it is a direct consequence of $PV = NkT$.

- we now return to the question of $(\partial U / \partial T)_P$ in the case of an ideal gas (for simplification of Eq. 45). Since the internal energy of a fixed quantity of an ideal gas can be written in a form that depends *only* on its temperature:

$$\left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V \quad \text{for an ideal gas} \quad (46)$$

and thus Eq. 45 simplifies to what is known as **Mayer's relation**:

$$C_P = C_V + Nk \quad \text{for an ideal gas.} \quad (47)$$

Since $Nk > 0$ this expression is consistent with the qualitative behaviour that we expect: as a gas expands at constant pressure it loses energy due to the mechanical work it is doing on its surroundings. Therefore it takes more heat to raise the temperature under constant pressure conditions as compared to constant volume conditions ($C_P > C_V$).

- we have been concentrating on ideal gases, but C_P can be measured for liquids and solids. Problem 1.46 of SITP is an important illustration of why C_V is not normally measured for solids. Later in the course (Section 25.3 and SITP Problem 5.14) we will derive a general expression (applicable to any material) for $C_P - C_V$ in terms of its isobaric thermal expansivity ($\beta := (1/V)(\partial V / \partial T)_P$) and isothermal compressibility ($\kappa_T := -(1/V)(\partial V / \partial P)_T$) — a triumph of classical macroscopic thermodynamics.

7 Intensive and extensive thermodynamic variables (SITP 5.2)

- notice that in Fig. 5, C_V was “normalized” by Nk , since we wanted to consider a quantity that was independent of the specific amount of material. That is a general idea; more specifically, the thermodynamics of most systems show a trivial dependence on their size once they are large enough.
- for example if we combine two volumes of water (V_1 and V_2) each at the same temperature and pressure, the combined system “at the temperature and pressure” will have volume $V_1 + V_2$, energy $U_1 + U_2$, number of particles $N_1 + N_2$, and so on.
- this notion may be formalized by classifying thermodynamics variables as *intensive* or *extensive* (most, but not all, thermodynamic variables can be classified this way):
 - **intensive variables** are those which remain the same as system size is changed while the system’s temperature and pressure are kept constant. By this definition, temperature and pressure are themselves intensive.

²²We might have anticipated that U/N for an ideal gas depends only on temperature, since all of the C_V ’s shown in Fig. 5 are shown as functions of temperature *alone*. That U/N is only a function of T for a monatomic gas (at low temperatures) is obvious from $U = N\frac{3}{2}kT$.

- **extensive variables** are those which scale linearly with system size (volume) while the system's temperature and pressure are kept constant. Examples are volume, entropy, energy, etc...
- more formally, if a given thermodynamic system exists, described by the variables²³

$$P, T, U, V, S, \text{etc}...,$$

then any other system, with

$$P' = P, T' = T, U' = \alpha U, V' = \alpha V, S' = \alpha S, \text{etc}...,$$

is also a valid physical system, where α is a positive constant, and the system sizes (V and αV) are “large enough”. i.e., in the extreme it is meaningless to consider a system of one atom as it would lack any contribution to its energy from interatomic potentials. Only once a system size exceeds a certain threshold, will its extensive properties scale reliably with size (to within a certain tolerance). Similar considerations apply to surface energies etc...

- based on these definitions, it is straightforward to establish some rules for determining whether or not variables defined using combinations of thermodynamic variables are intensive or extensive.
- for example, the ratio of two extensive quantities is intensive.
i.e., $\frac{E_1}{E_2}$ becomes $\frac{\alpha E_1}{\alpha E_2} = \frac{E_1}{E_2}$, so that generally

$$\frac{\text{extensive}}{\text{extensive}} \text{ is intensive} \quad (48)$$

and similarly

$$\text{extensive} \times \text{intensive} \text{ is extensive} \quad (49)$$

- as an example, heat capacity is extensive. But if we normalize by the amount of mass, the result is intensive. It is customary to refer to the normalized heat capacity (C_P/m or C_V/m) as the **specific heat capacity**. If we normalize by the number of moles of the material, the result (C_P/n or C_V/n) is also intensive, and referred to as **molar specific heat capacity**.
- be wary of any expression that you have derived that involves adding or subtracting intensive quantities from extensive ones. It is almost certainly incorrect.

8 Expansion and compression work (SITP 1.5)

8.1 General considerations

- this piston/weight combination of Section 6 was chosen for concreteness.

²³We have not discussed the definition of entropy S yet, but include it here for future reference.

- work is done by *any* system expanding with a *well-defined pressure* (this condition excludes Joule's experiment with the two cylinders — I will say more about this shortly).
e.g., consider a volume of gas within a membrane (of negligible elasticity), that is at constant pressure, but expands its volume due to heating of the gas within (raising its temperature):



The work done *on* the gas within the membrane is:

$$W = -P\Delta V \quad (50)$$

and the corresponding work done on the surrounding atmosphere is $P\Delta V$. The shape of the object before and after can be arbitrarily complex.

- if P changes with V , the generalization of Eq. 50 is

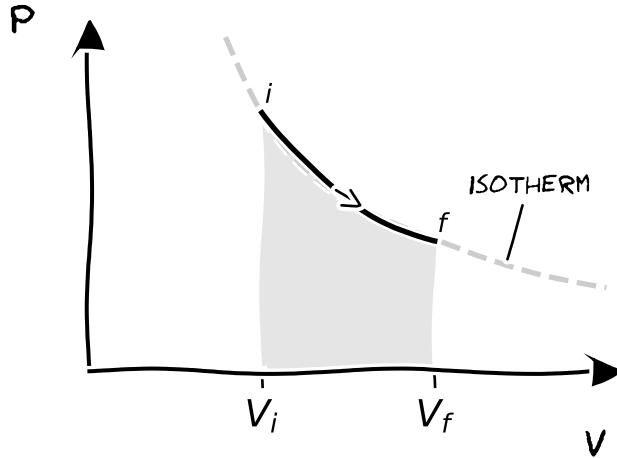
$$W = - \int P dV, \quad (51)$$

where the limits of the integral are determined by the process under consideration, and P is a function of V . The specific function depends on the process considered.

8.2 Isothermal expansion/compression of an ideal gas

- a simple example of the usage of Eq. 51 is given by the **isothermal** expansion/compression of an ideal gas: a gas is expanded/compressed with work being done. Heat flows from a surrounding environment into or out of the gas in order to maintain it at the *same (iso)* temperature as the surroundings.
- to make this example concrete, imagine pulling a party balloon under water *slowly enough* so that the gas inside the balloon stays at the same (constant) temperature as the surrounding water. Work is done on the gas ($W > 0$) inside the balloon as it is pulled deeper into the water i.e., pressure increases with water depth (Section B) and thus the volume of the gas decreases if it stays at the same temperature, so that $W = - \int P dV > 0$. The gas inside expels heat, $Q < 0$, so as to compensate the work done on gas $W > 0$, for a net $\Delta U = Q + W = 0$; i.e., $\Delta U = 0$ ensures $\Delta T = 0$ for an ideal gas.
- we will analyze isothermal (and other) processes using **indicator diagrams**,²⁴ plots of P versus V :

²⁴Indicator diagrams date back to the steam locomotive era. They were automatically generated to monitor and improve engine efficiency.



The shaded area shown above is $-W_{\text{mech}}$:

$$-W_{\text{mech}} = \int_{V_i}^{V_f} P dV. \quad (52)$$

Using the ideal gas law:

$$W_{\text{mech}} = - \int_{V_i}^{V_f} \frac{NkT}{V} dV \quad (53)$$

$$= -NkT \ln(V) \Big|_{V_i}^{V_f} \quad (54)$$

$$= -NkT \ln(V_f/V_i). \quad (55)$$

Since the temperature remains constant in this process, the only work being done is expansion/compression work. Also, since we are considering an ideal gas: $\Delta U = 0$ (remember Joule's experiment). The first law of thermodynamics $\Delta U = Q + W$ then tells us that $Q = -W$:

$$Q = NkT \ln(V_f/V_i) \quad (56)$$

- if $V_f > V_i$ (expansion) then $\ln(V_f/V_i) > 0$, and thus heat will flow *from* the surroundings *into* the system ($Q > 0$), whereas heat will flow *from* the system to the surroundings ($Q < 0$) if $V_i > V_f$ (compression).
- now let us consider that the same transformation from i to f could be made in *different* ways:

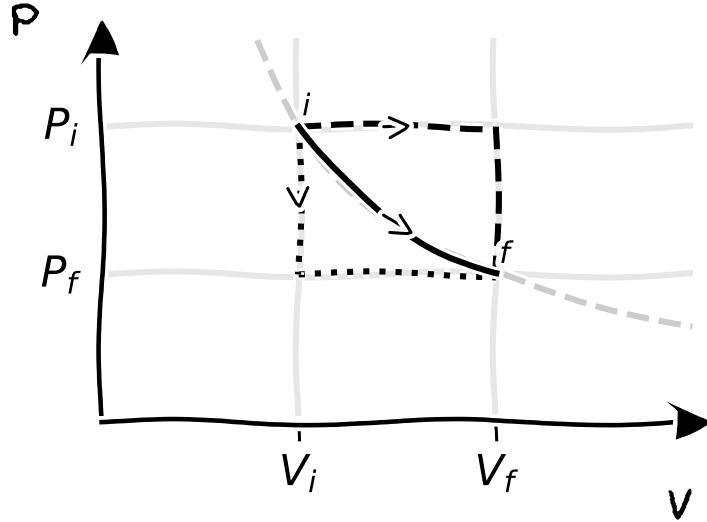


Figure 8: Three different paths with the same initial i and final f conditions.

Processes in which pressure remains constant are known as **isobaric**. Processes in which volume remains constant are known as **isochoric**. The corresponding straight lines on an indicator diagram are known as isobars and isochores.

Since volume does not change in an isochoric process, no expansion/compression work is done.

For concreteness, will consider that special case that the volume doubles ($V_f = 2V_i$) and pressure halves ($P_f = \frac{1}{2}P_i$) as we go from i to f . By the ideal gas law, the temperatures of the gas at i and f will be the same. It follows from the discussion of Joule's experiment that $\Delta U = 0$ between A and B .

For the path (isochoric followed by isobaric):

No work is done in the first step, as it is isochoric. We may integrate to determine the work done during the isobaric second step:

$$W = - \int_{V_i}^{V_f} P dV \quad (57)$$

$$= -P_f \int_{V_i}^{V_f} dV \quad (58)$$

$$= -P_f (V_f - V_i) \quad (59)$$

and with $V_f = 2V_i$ and $P_f = P_i/2$:

$$W = -\frac{P_i}{2}V_i. \quad (60)$$

Since $\Delta U = 0$, we have $Q = -W$, and thus

$$Q = \frac{P_i}{2}V_i \quad (61)$$

(From this example we see that the mechanical work done on a system in an isobaric process is $W = -P\Delta V$, where ΔV is the change in volume of the system.)

For the ----- path (isobaric followed by isochoric):

The work done in the isobaric first step is

$$W = -P\Delta V \quad (62)$$

$$= -P_i(V_f - V_i) \quad (63)$$

and with $V_f = 2V_i$:

$$W = -P_iV_i. \quad (64)$$

No work is done in the second step, as it is isochoric. Again, since $\Delta U = 0$, we have $Q = -W$, and thus

$$Q = P_iV_i. \quad (65)$$

For the isothermal path:

We use Eq.'s 55 and 56 with $V_f/V_i = 2$, and the ideal gas law, to obtain:

$$W = -NkT \ln(V_f/V_i) \quad (66)$$

$$= -P_iV_i \ln 2 \quad (67)$$

and

$$Q = P_iV_i \ln 2. \quad (68)$$

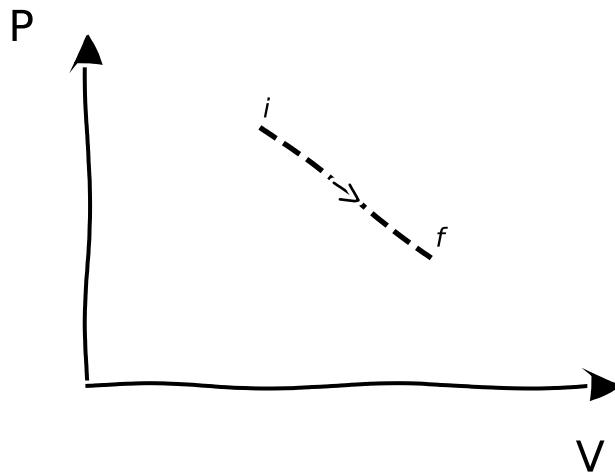
Note that although $\Delta U = 0$ for any process that goes from A to B, the work done on the gas W and the heat flow into the gas Q are different for all three paths (○○○, ⋯; Eq.'s 61 65 68, respectively). I cannot overemphasize that Q and W are related to processes, not(!) states. A system does not have a Q or a W and that is why we never use symbols such as dW and dQ to represent infinitesimal W 's and Q 's.²⁵ Nor do we ever use ΔQ or ΔW . On the other hand dU and ΔU are perfectly valid and we use them all the time, as U is a function of the state of the system, and thus its difference between two states is well-defined and independent of how we have “travelled” between the two states.

Example: SITP Problem 1.31

-
- how do we represent Joule's experiment (Fig. 7) on an indicator diagram? Remember that in this experiment a gas expands into twice the volume *but does no work*.

²⁵Other authors use the symbols dQ and dW to signify so-called **inexact differentials** (note the presence of the bars). SITP wisely avoids this usage (see the footnote on page 18 of SITP), as will I, viewing it as unnecessarily formalizing what is (ultimately) a rather straightforward concept (your opinion may differ). Once you are clear about the physics, digesting other references — that do use this notation — will be straightforward.

- we *cannot* represent this process on an indicator diagram. The system does not have well-defined pressure, volume and temperature while it is expanding. It is not in “equilibrium” and cannot be described by an equation of state (such as the ideal gas law). It is customary to connect the initial and final states with a dashed line:



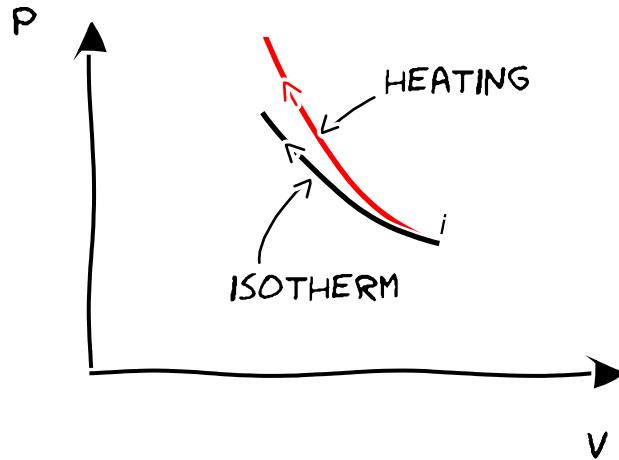
- processes such as those shown in Fig. 8 where the system *does* pass through a series of equilibrium states (i.e., has a well defined pressure, volume and temperature) are known as **quasi-static processes**. The gas expansion in Joule’s experiment is **not** a quasi-static process: we cannot write $W_{\text{mech}} = - \int P dV$. As noted above, these non-quasi-static processes can be schematically indicated by drawing a dashed line between the initial and final states. However, we must not attribute any meaning to the path of the dashed line between the points.

8.3 Adiabatic and quasi-static expansion/compression of an ideal gas



- in isothermal expansion/compression of an ideal gas it is important that heat flows into/out-of the gas to maintain a constant temperature. This heat flow may not occur if the process happens sufficiently quickly or system is thermally insulated (or some combination thereof). A process (either quasi-static or not) in which no heat flows is **adiabatic**,²⁶ i.e., $Q = 0$.
- if we compress a gas, disallowing heat flow out of the gas, we expect its temperature to rise:

²⁶ Unfortunately the terminology of SITP is not completely standard. Other books consider “adiabatic” to refer only to *quasi-static* processes in which no heat flows (as we shall discuss later, it is more precise to refer to these as *isentropic* processes). For example, SITP would consider Joule’s free expansion experiment (Fig. 7) to be adiabatic, whereas it is not under the alternate definition of other authors.



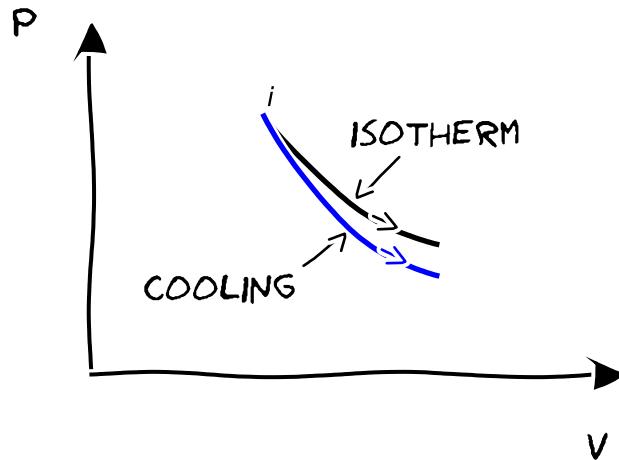
i.e., with $Q = 0$, the first law is $\Delta U = W$, so that if $W > 0$, as for compression, $\Delta U > 0$, and thus temperature rises. By the way, we use the term **adiabats** for these curves on indicator diagrams corresponding to quasi-static adiabatic compression/expansion.

This temperature increase is observed when using a bicycle pump. The body of the pump gets warm because the compression of the air heats the gas relatively quickly, before it has a chance to reach thermal equilibrium with the pump body and surroundings. Since the walls are not perfectly insulating heat does eventually flow out of the air, heating the pump body.

But a much more lively example is that of the so-called “fire-piston/syringe”:

<https://youtu.be/4qe1Ueifekg>

- we might also expect that when a gas expands, *doing work* on the outside world, the gas temperature will go down.



This type of cooling upon expansion can cause condensation, as nicely illustrated in [this demo](#).

- these predictions/observations regarding adiabatic, quasi-static expansion/compression will now be made quantitative. Our three ingredients will be:

- (1) the first law with $Q = 0$,
- (2) the ideal gas law, and
- (3) the assumption of a temperature independent heat capacity C_V . Gases having this property are **sometimes** referred to as being **calorically perfect**. As Fig. 5 shows, heat capacities are generally not temperature independent. However, it can be a reasonable approximation over a limited temperature range.

- starting from the first law:

$$dU = Q + W \quad (69)$$

and setting $Q = 0$ yields:

$$dU = W. \quad (70)$$

In elementary calculus dU is “illegal”. Think of it — temporarily — as being a small increment. And likewise for dV and dT in what follows.

For a quasi-static process:

$$dU = -PdV. \quad (71)$$

For an ideal gas (only!), the change in energy dU is simply related to the change in temperature by:

$$C_VdT = -PdV. \quad (72)$$

Using the ideal gas law in Eq. 72:

$$C_VdT = -\frac{NkT}{V}dV. \quad (73)$$

Rearranging gives:

$$C_V \frac{dT}{T} = -Nk \frac{dV}{V}. \quad (74)$$

Now let us consider what dU , dV and dT *really* mean. We are interested in a particular path on an indicator diagram. We could parameterize that path by a variable; call it λ . The start of the path (initial conditions) could be $\lambda_i = 0$ and the finish (final conditions) could be $\lambda_f = 1$. All of the P , V , T , and U can be considered functions of λ as they vary along the path. In this way of thinking Eq. 76 may be considered to be equivalent to

$$C_V \frac{1}{T} \frac{dT}{d\lambda} = -Nk \frac{1}{V} \frac{dV}{d\lambda}, \quad (75)$$

which is much more mathematically respectable!²⁷

²⁷ The appearance of isolated dU 's, dV 's, etc... might make you feel a bit queasy. Thinking of them all as derivatives with respect to single variable parameterizing the path pacifies me. I strongly recommend this outlook and will return to it repeatedly throughout these notes. Note — as in this derivation — the specifics of the parameterization do not actually matter — somewhat vindicating the dU , dV , etc..., shorthand. Time can be taken as the parameteric variable if one wishes a physical interpretation. For completeness, I note that there is a more elaborate “differential forms” interpretation of the “isolated” dV 's, dT 's and so-on. Further information and debate on the utility of the differential forms interpretation can be found [here](#) and [here](#).

Making use of $d \ln x / dx = 1/x$ and the chain rule, recalling that we are assuming C_V is a constant:

$$C_V \frac{d \ln T}{d \lambda} = -Nk \frac{d \ln V}{d \lambda}. \quad (76)$$

Rearranging gives:

$$\frac{d}{d \lambda} (C_V \ln T + Nk \ln V) = 0. \quad (77)$$

Thus $C_V \ln T + Nk \ln V$ is constant along the path, as λ varies. Equating its value at the initial and final conditions:

$$C_V \ln T_i + Nk \ln V_i = C_V \ln T_f + Nk \ln V_f \quad (78)$$

and rearranging gives

$$C_V \ln \left(\frac{T_f}{T_i} \right) = -Nk \ln \left(\frac{V_f}{V_i} \right) \quad (79)$$

Solving for the temperature ratio:

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{-\frac{Nk}{C_V}}. \quad (80)$$

Recall that $C_P - C_V = Nk$, so that it is useful to define the **adiabatic exponent** as²⁸

$$\boxed{\gamma := \frac{C_P}{C_V}} \quad (82)$$

and then Eq. 80 can be written as

$$\boxed{\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma}} \quad (83)$$

This result also readily gives us the form of adiabats on the indicator diagram. Using the ideal gas law on the LHS of Eq. 83 gives:

$$\frac{P_f V_f}{P_i V_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma} \quad (84)$$

which may be rearranged to give

$$\boxed{\frac{P_f}{P_i} = \left(\frac{V_f}{V_i} \right)^{-\gamma}} \quad (85)$$

²⁸Instead of γ , SITP writes his results in terms of the f that appears in the equipartition theorem. Again, I do not like the emphasis that SITP places on the equipartition theorem. For comparison with some of the results in SITP, note the correspondence $\gamma = 1 + 2/f$ and $f = 2/(\gamma - 1)$, obtained from $C_P - C_V = Nk$ and $C_V = f Nk/2$; e.g., Eq. 502 may be written as

$$U = \frac{2}{(\gamma - 1)} \frac{1}{2} NkT. \quad (81)$$

The advantage of SITP's use of f is that the equipartition theorem makes some special values easy to remember; e.g., $f = 3$ for a monatomic gas. However, I prefer to express the results for adiabatic expansion/compression using γ since its usage is more common than f .

This is a form convenient for comparison with a similar one for isothermal expansion and compression:

$$\frac{P_f}{P_i} = \left(\frac{V_f}{V_i} \right)^{-1}. \quad (86)$$

The definition of γ (Eq. 82) makes it clear that $\gamma > 1$. Thus the pressure falls off more quickly with increasing volume in the adiabatic case as compared to the isothermal case.

- two important special cases for γ are:

- (1) a monatomic gas: $\gamma = 5/3$, which follows from $C_V = \frac{3}{2}Nk$ (i.e., $f = 3$) and Eq. 47, and
- (2) a diatomic gas at room temperature: $\gamma \approx 7/5$, which follows from $C_V \approx \frac{5}{2}Nk$ (i.e., $f = 5$; recall the discussion in Section 5) and Eq. 47.

Example: SITP Problem 1.37

9 Introduction to phase transitions (SITP 1.6)

9.1 Deviations from the ideal gas law

-
- the ideal gas holds a special status in our study of thermal physics. In example problems we repeatedly use the ideal gas law and assume that any deviations are insignificant. Later — in Part II — it will be one of our toy systems for understanding the formal definition of temperature. From a certain point of view, the fact that no gas is *truly* ideal is not particularly important to the study of thermal physics. Nonetheless, a complete suppression of curiosity in the imperfections of models — although common — is not healthy for a physicist. That alone would be sufficient reason for studying deviations from the ideal gas law; but we also have another: clearly the ideal gas law must break down so as to allow the formation of both liquids and solids. In other words we *know* that the ideal gas law is a completely inadequate equation of state for liquids and solids. Studying deviations from the ideal gas law provides a means by which to introduce these different **phases**²⁹ of matter and the corresponding **phase transitions** between them.
- to make things concrete I will use diatomic nitrogen as an example because 1) it is the largest constituent of air, and thus will give us *some* insight into the behaviour of air, and 2) its liquid phase is relatively familiar, frequently making an appearance in science demos; e.g., liquid nitrogen ice-cream.
- let us begin in familiar territory by examining pure nitrogen near room temperature $T = 300\text{ K}$ and at atmospheric pressure $P = 1\text{ bar}$. Under these conditions nitrogen gas occupies volume

²⁹The usage of the term “phases” is preferred to “states of matter” because: 1) it is more specific e.g., carbon can be in the “solid-state” but in either the diamond *phase* or graphite *phase*; and 2) to avoid confusion, as we will be discussing both thermodynamic and quantum mechanical *states* of systems. The phase concept will become clearer in Part III of these notes, where we will be able to quantify the conditions for phase transitions to occur (see Section 23.3).

is a factor of ≈ 0.9998 smaller than one would expect from the ideal gas law. Decreasing pressure (while keeping T constant) is only expected to improve agreement. The more interesting route is to increase pressure, thereby decreasing the volume. Surely there must be a limit to the volume that we can squeeze a fixed number of nitrogen molecules into, based on the “size” of a nitrogen molecule?

- the following is the first of a series of plots of *real* nitrogen isotherms that I will show, calculated using the CoolProp computer code, which allows evaluations of equations of state based on data from the literature (see Appendix G):

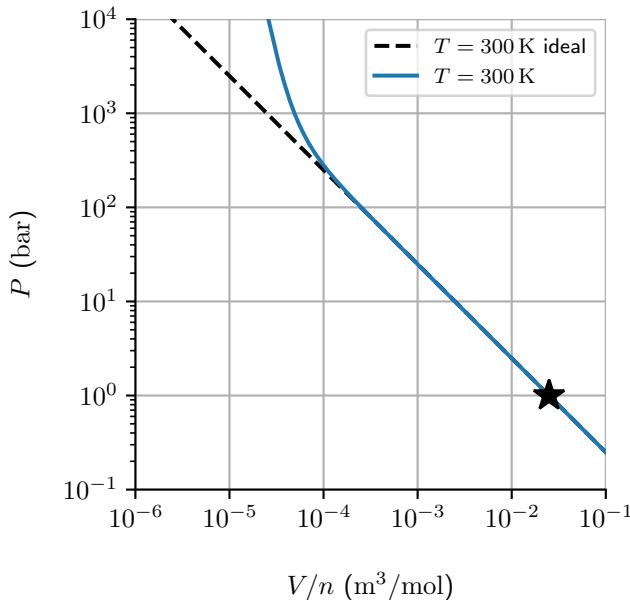


Figure 9: An ideal gas isotherm and a real isotherm for N₂. The quantity V/n is known as the **molar volume**; i.e., the volume of one mole. At low molar volumes the pressure rises above that predicted by the ideal gas law because it gets more difficult to compress the nitrogen into an arbitrarily small volume — the molecules themselves occupy a volume. The \star indicates “standard conditions” of $T = 300\text{ K}$, $P = 1\text{ bar}$, where agreement with the ideal gas law is very good. See Problem 1.17 of SITP (recommended) for one method for characterization small deviations from the ideal gas behaviour.

The rise in pressures at low volume is entirely consistent with the idea that there will be a resistance to squeezing molecules close together once they are separated by distances on the order of their size. But it is also true that at larger distances molecules will *attract* rather than repel. Is there any evidence of that attraction in the real isotherm? Well perhaps slightly: as was mentioned the occupied volume at 1 bar is *smaller* than that predicted by the ideal gas. But it is a small effect, not discernible in Fig. 9.

A related surprise is that there is no evidence (at least over the range of the plot in Fig. 9) that either a liquid or solid forms. We might expect some sort of discontinuity relating to phase transitions, but none is present. Let us now consider isotherms away from room temperature:

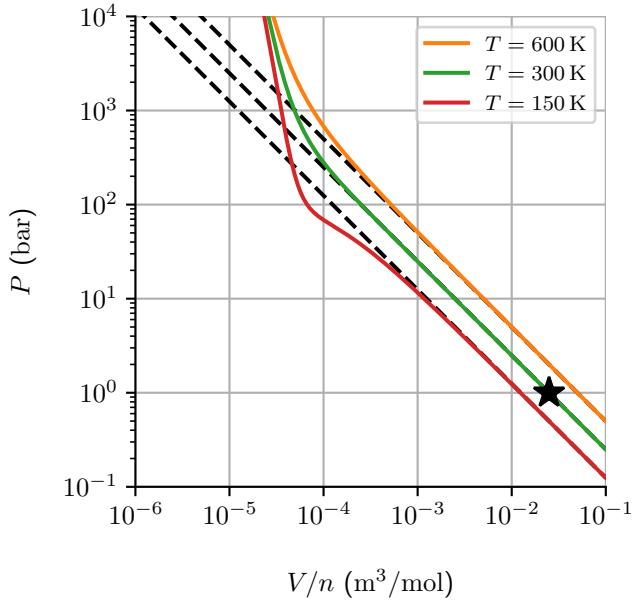
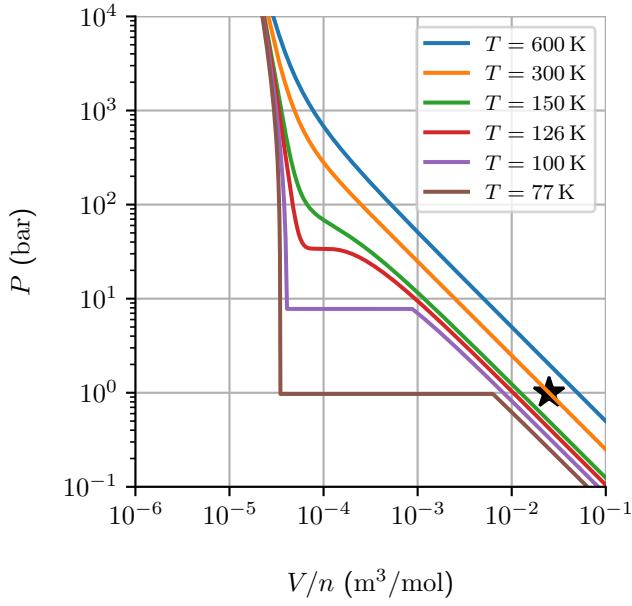


Figure 10: Ideal and real gas isotherms for N_2 . The ideal gas law predictions are the dashed lines.

The plot indicates that the higher temperature $T = 600 \text{ K}$ isotherm does not differ in any qualitative way from the $T = 300 \text{ K}$ isotherm. The $T = 150 \text{ K}$ is more interesting: note that at $V/n \approx 1 \times 10^{-4} \text{ m}^3$ the molar volume dips *below* the ideal gas prediction, before rising at lower volumes. The $T = 150 \text{ K}$ isotherm illustrates both the attractive and repulsive nature of the interaction between the molecules. Thus we expect that lower temperatures are where the interesting stuff is going to happen:

Figure 11: Real gas isotherms for N_2 .

As anticipated, the “dip” becomes more prominent at even lower temperatures. In fact at about $T = 126\text{ K}$ we see a sort of inflection point, beyond which we might guess that perhaps pressure would even *decrease* with smaller volumes. It is worth pondering over why that pressure decrease would be problematic³⁰ — if it occurred. And in fact, as the isotherms at $T = 100\text{ K}$ and $T = 77\text{ K}$ show, this “inflection” does not happen. Instead the pressure is *constant* over a range of volumes. We are no longer in Kansas.

What is going on? Why does the pressure remain constant over a range of volumes? We are in fact observing is that two phases — liquid and gas — can be in mechanical equilibrium with one another (i.e., the same pressure), but there can be varying amounts of each phase present. At higher volumes all of the N_2 is in gaseous form. As we proceed to lower volumes this gas is progressively converted into liquid. Once all of the N_2 is in liquid form it then becomes quite difficult to compress; i.e., the near vertical lines at around $V/n \approx 3 \times 10^{-5} \text{ m}^3/\text{mol}$.

It is customary to indicate the boundary of the liquid-gas **coexistence** region with a line:

³⁰Think mechanical stability.

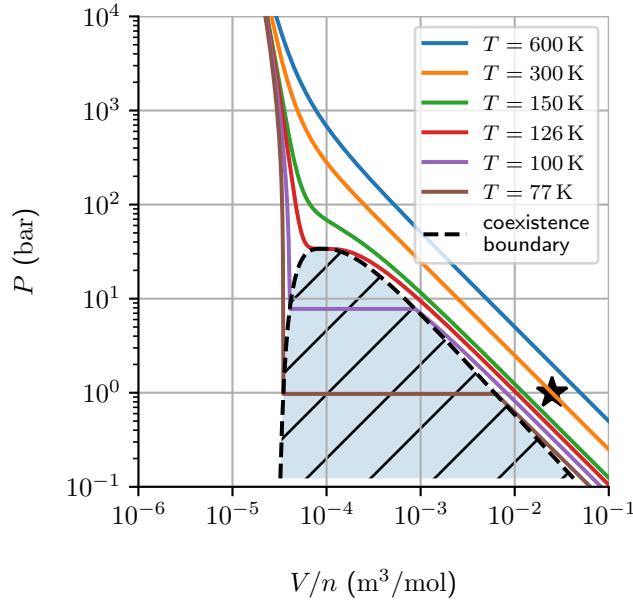


Figure 12: Real gas isotherms for N_2 , with the liquid-gas coexistence region shaded and its boundary indicated with the dashed line.

Since the liquid-gas phase transition occurs at a well-defined pressure for each isotherm, it is natural to consider plotting this “transition pressure” versus temperature:

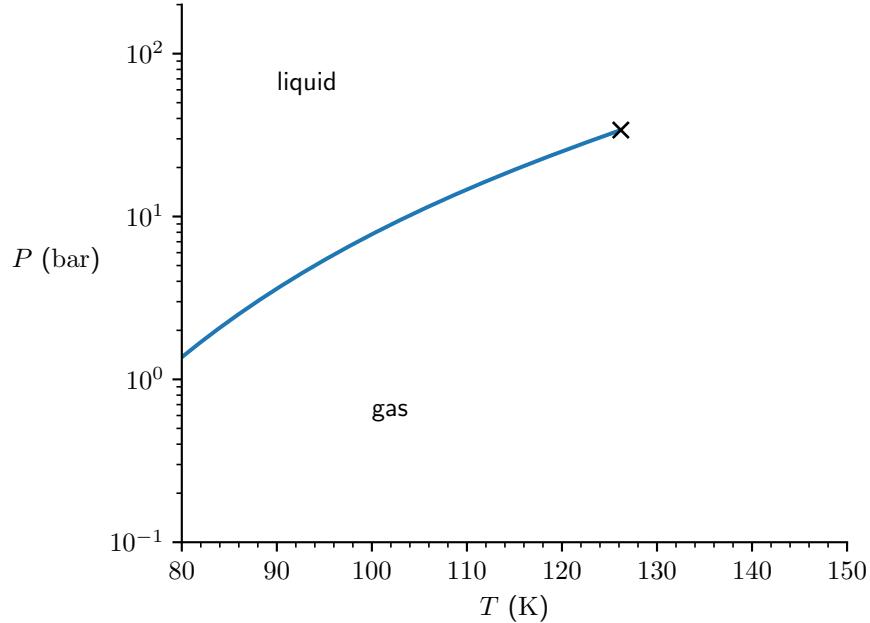
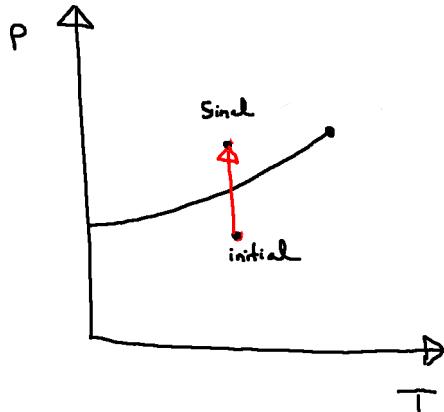
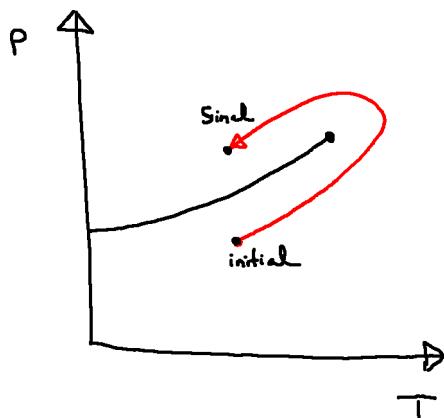


Figure 13: The transition between liquid and gas phases of N_2 . The extent of the plot has been limited so as to avoid considering the solid phases (yet). The endpoint (\times) is known as the **critical point**

The region on the higher pressure side of the line corresponds to the liquid phase and the region on the lower pressure side corresponds to the gaseous phase. But there is a problem with this classification: recall that these pressure “plateaus” only actually occurred below a certain temperature (and pressure). Suppose first that we take a “direct” isothermal path, for which a discontinuous change in volume will be observed as we cross the phase boundary:



Now consider instead that one could change the pressure and temperature in a way that traces out a path that never crosses the boundary:



In this manner we would be continuously changing a gas into a solid, *without* any discrete jump in volume.

- this skirting around the phase boundary shows us that liquids and gases are not really fundamentally different. That is why we sometimes refer to them collectively as **fluids**.³¹
- what about solids? We might expect that if N₂ is cold enough it will “freeze”, forming a solid:

³¹In high school they told me how liquids and gases were different from one another. I always thought the supposed differences lacked firmness — in the sense that these differences were just a matter of degree. In contrast, it is clear how a solid is different from a fluid: in the solid phase, atoms or molecules are fixed in their relative arrangement in space. But no similarly sharp criteria allow liquids and gases to be distinguished. It all makes sense to me now.

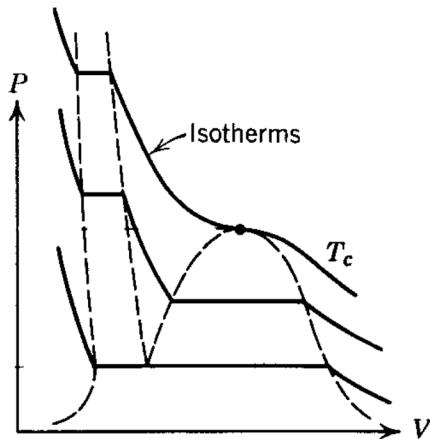


Figure 14: A “cartoon” indicating the plateaus associated with liquid to solid transitions (in addition to gas to solid transitions). Source: Figure 2.2 from K. Huang, *Statistical mechanics*, 2nd ed (Wiley, New York, 1987).

- if we increase the extent of our Fig. 13, adding lines where there is a discrete change in the properties of N_2 , we also find two additional “boundaries” between phases: 1) one between the solid and liquid phases and 2) another between the solid and gas phases.

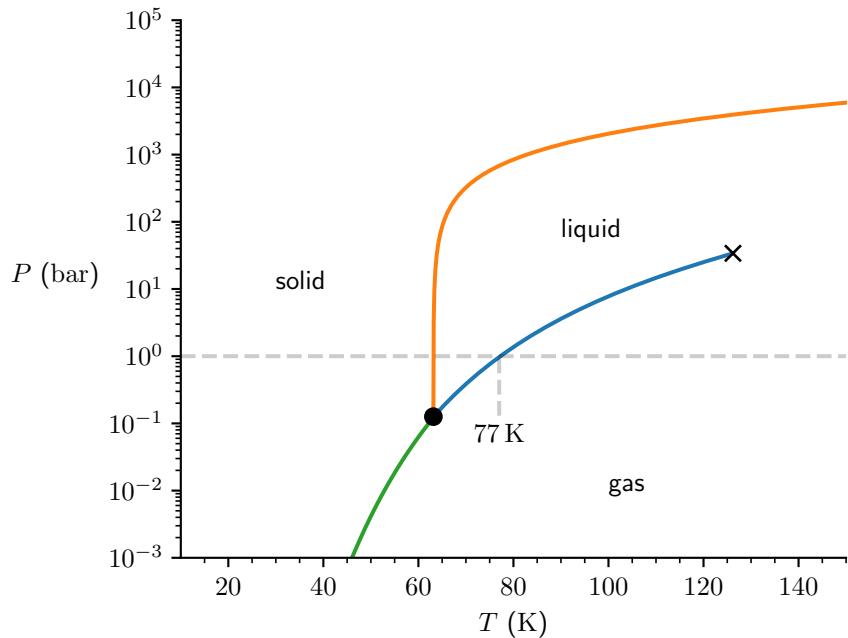


Figure 15: Phase boundaries for N_2 . The point where the three phase boundaries meet (●) is known as the **triple point**. The liquid gas transition of 77 K at 1 bar is identified, as it is a temperature that is frequently mentioned in association with liquid nitrogen.

Figure 15 is our first example of what is known as a **phase diagram**: a graphical indication of the phases that are favoured under varying conditions (typically temperature and pressure).

9.2 Latent heats

-
- there are a few customary designations for phase transitions based on “what direction” we are travelling in:
 - (a) melting: solid \rightarrow liquid
 - (b) freezing: liquid \rightarrow solid
 - (c) boiling: liquid \rightarrow gas
 - (d) condensation:³² gas \rightarrow liquid
 - (e) sublimation: solid \rightarrow gas
 - (f) deposition: gas \rightarrow solid
- surprisingly heat can — and frequently must — flow in or out of a substance when it is undergoing a phase transition *without* the substance changing temperature.



- the **latent heat** of a phase transition is defined as

$$L_{1 \rightarrow 2} := Q \quad (87)$$

where Q is the heat flow *into* the system during the phase transition from phase 1 to phase 2. ³³ During the phase transition, the system should

1. be at constant pressure, and
 2. only do (or have done on) expansion/compression work.
- latent heats are a function of pressure.
 - for water at $P = 1$ bar:
 - (a) melting: $L_{\text{melting}}/m \approx 333 \text{ J/g}$
 - (b) boiling: $L_{\text{boiling}}/m \approx 2260 \text{ J/g}$

³²The term “liquefaction” (or **liquification**) seems — by convention — to cover the case of both melting and condensation.

³³**Warning:** SITP defines the latent heat differently: $L := Q/m$ (his Eq. 1.50) where m is the mass of the material. Later he also uses *molar latent heat*: $:= Q/n$, where n is the number of moles of material. His usage of symbol L is inconsistent. For example, his Eq. 5.47 uses L as we have defined in Eq. 87 (as also defined by Blundell and Blundell, *Concepts of thermal physics*, 2nd ed., pg 321). For consistency, $L := Q/m$ should be known as the *specific* latent heat.

- to get a feeling for these numbers, consider the **specific heat capacity** (heat capacity normalized by mass) of water: $C_P/m \approx 4.2 \text{ J}/(\text{g} \cdot \text{K})$ at $P = 1 \text{ bar}$. Using $Q/m = \Delta T \times C_P/m$ we may estimate that to heat liquid water from 0°C to 100°C requires $Q/m \approx 420 \text{ J/g}$. This value is much smaller than $L_{\text{boiling}}/m \approx 2260 \text{ J/g}$.
- steam burns are serious because of the large latent heat for boiling — when steam condenses on your skin, heat flows into your skin not only due to cooling from 100°C , but also due to the initial condensation. Since condensation is the opposite of boiling, the heat flow *out of* the water into your skin is given by L_{boiling} .

Example: SITP Problem 1.47, Cooling tea with ice

- we will have more to say about phase transitions in Part III. In particular once we understand temperature and entropy from the fundamental point of view, we will be able to say quantitative things about the boundaries between phases. Again — in the spirit of this introductory part of the notes — it is helpful to familiarize ourselves with the basic phenomenology first.

10 Enthalpy (SITP 1.6)

10.1 General considerations

- the **enthalpy** of a system is defined as

$$H := U + PV \quad (88)$$

- enthalpy has an interesting (but useless) physical interpretation.³⁴

Enthalpy is the total energy required to create a system U plus the energy required to “make room for it” ($\Delta V = V$) in a surrounding constant pressure environment: PV .

- a more useful physical interpretation relates to quasi-static processes that occur at constant pressures; e.g., system is surrounded by atmospheric pressure. In this case, changes in enthalpy tell us the heat flow in to/out of system, if the only work done is expansion/compression:

$$\Delta H = \Delta U + \Delta(PV). \quad (89)$$

Under constant pressure, $\Delta(PV) = P\Delta V$

$$\Delta H = \Delta U + P\Delta V. \quad (90)$$

Using the first law of thermodynamics:

$$\Delta H = Q + W + P\Delta V. \quad (91)$$

³⁴The “making room for it” interpretation of enthalpy ascribes significance to its absolute value. But that is difficult, because what should the *absolute* energy U be? Rest mass energy? As you shall see, it is *differences in and derivatives of* enthalpy that are of use.

If the only work done by the system is expansion/compression work at constant pressure, then $W = -P\Delta V$, and thus we have:

$$\Delta H = Q. \quad (92)$$

- often we do not care how much mechanical work is done; we just care about heat flow. In these situations enthalpy is useful.
- recall that our previous definition of C_P was a bit awkward (i.e., Eq. 38, in which we needed to specify a *process* to define Q). Equivalently, but more precisely, we may now define C_P as a state function, without any reference to a process:

$$C_P := \left(\frac{\partial H}{\partial T} \right)_P \quad (93)$$

resembling our definition of C_V :

$$C_V := \left(\frac{\partial U}{\partial T} \right)_V. \quad (94)$$

- likewise the latent heats for transitions (e.g., melting and boiling) are really best defined as “jumps” in enthalpy:

$$L_{1 \rightarrow 2} := H_2 - H_1. \quad (95)$$

This definition is consistent that of Eq. 87 (the reasoning being identical to that for C_P).

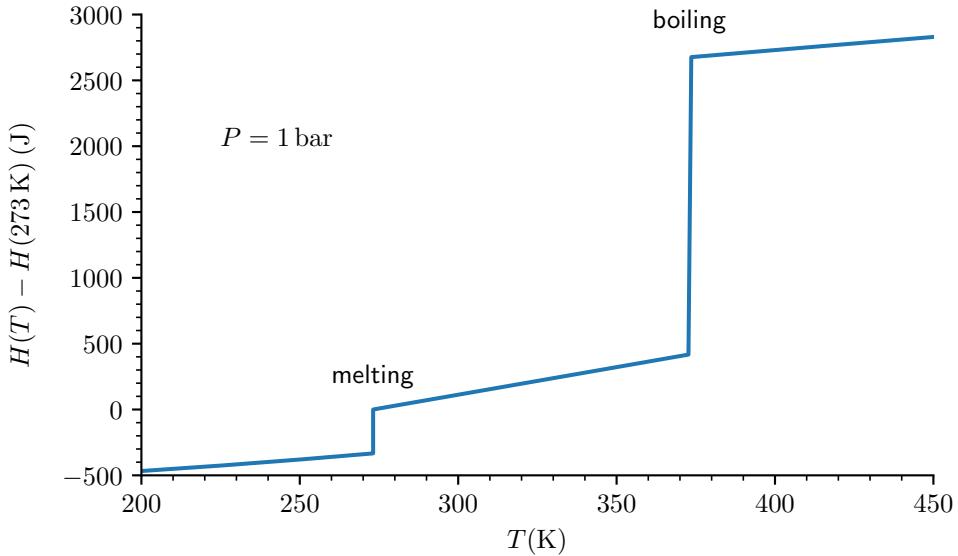


Figure 16: The enthalpy of 1 g of water as a function of temperature at $P = 1$ bar. The discrete jumps correspond to the latent heats of melting and boiling. The slopes correspond to C_P .

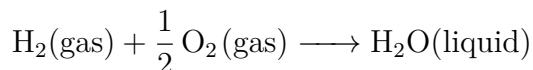
10.2 Changes in enthalpy for chemical reactions

- the reference data section of SITP gives the **enthalpies of formation** of various compounds. The enthalpy of formation for a given compound is defined as the difference in the enthalpy between 1 mol of the compound and its constituent elements in their most stable states at room temperature and pressure. It is normally quoted for 1 mol of the compound of interest.

e.g.,

$$\Delta_f H(\text{H}_2\text{O}(\text{liquid})) = -286 \text{ kJ}$$

corresponding to the change in enthalpy ($H_{\text{products}} - H_{\text{reactants}}$) for the reaction:



in which 1 mol of H_2O is made.

- the $\Delta_f H$'s for most compounds are negative i.e., heat is released in forming them from their elemental constituents.
- by definition

$$\Delta_f H(\text{O}_2) = \Delta_f H(\text{H}_2) = 0$$

since these molecules are already in their most stable elemental form.

- the enthalpies of formation are useful as the change in enthalpy for *any* chemical reaction can be established if the enthalpies of formation of all of the reactants and products are known. This change in enthalpy corresponds to the heat that flows *into* the system, provided the reaction takes place at constant pressure and the only work done by/on the system is expansion/compression work.

Examples: SITP 1.49, Combustion to make water, SITP Problem 1.51, Combustion of glucose

11 Thermal conductivity (SITP 1.7)

11.1 Introduction

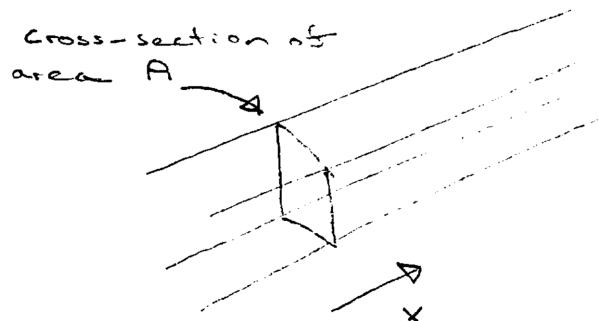
- let us briefly discuss the *rate* of heat flow, part of the general field of **heat transport**.³⁵
- heat transport can occur by
 - (1) conduction
due to “direct contact at the molecular level” (SITP). Occurs in solids and fluids.

³⁵ A bit of semantics that you may safely ignore: thermodynamics and statistical mechanics normally only consider whether or not processes can happen, not the rate at which they happen; e.g., although we have discussed the heat released in chemical reactions, and we later discuss whether or not they can occur at all, we will not be discussing the rate at which reactions occur. Nonetheless, the rates of processes for which temperature is relevant *do* fall under the purview of the more general term: **thermal physics**. In this course, our small study of thermal conduction is justified by both its importance and absence elsewhere in the curriculum. And of course, thermal conductivity influences our perceptions of temperature: <https://youtu.be/vqDbMEdLiCs>

- (2) thermal radiation
(e.g., the earth is heated by the sun)
- (3) convection
important in our atmosphere (hot air rises); dominant in fluids; doesn't occur in solids.
- in the following sections we will briefly discuss conduction. Thermal radiation is studied in Part IV (normally optional in Phys 358). Convection is quite complicated and involves fluid dynamics; so we will not quantitatively discuss associated rates. However Problem 1.40 of SITP (recommended) considers the "threshold" temperature gradients required for convection, which are quite important to understanding the earth's atmosphere.

11.2 Fourier's law of heat conduction

-
- Fourier's law of heat conduction is notable for its role in the development of mathematics. The short "physics" treatment here will be complementary to the related techniques that you will learn in mathematical physics.
-
- we will concentrate on the case where the temperature varies in just one spatial direction, namely the 1-D case, just mentioning 3-D generalizations.
- imagine a long square bar:



where temperature is a function of position x along bar.

- the heat flowing across any square cross section of the bar is

$$\underbrace{\dot{Q}_x}_{\substack{\text{rate of} \\ \text{heat flow across} \\ \text{cross-section flowing} \\ \text{towards the } x}} = -k_t A \frac{dT}{dx}$$

\downarrow

thermal conductivity
 a property of the
 material

(96)

- this is Fourier's law of heat conduction.³⁶ The general 3-D version is

$$\frac{\vec{J}}{T} = -k_t \vec{\nabla} T$$

\uparrow
 heat per
 unit time
 per unit area

$\vec{\nabla} = \left(\hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} + \hat{z} \frac{\partial}{\partial z} \right)$

(97)

which reduces to Eq. 96 if there is only temperature variation in the x -direction.

- the thermal conductivities of common materials vary by orders of magnitude (pg 39 of SITP):³⁷

material	$k_t (\frac{W}{m \cdot K}) @ 300K$
air	0.026
wood	0.08
water	0.6
glass	0.8
iron	80
copper	400

take care in
 liquids; convection
 is normally more
 important

~ stainless steel is
 a poor conductor

³⁶Beware: in these notes I follow SITP and use k_t for the thermal conductivity (or k_1, k_2, \dots , for layers), k for Boltzmann's constant, and κ_T for the isothermal compressibility.

³⁷A more comprehensive table of thermal conductivities, including their dependencies on temperature, is given in Appendix A of the book: Lienhard and Lienhard, *A heat transfer textbook*, 5th ed.

- now let us consider a straightforward example from SITP (pg 39):
Suppose that we have a 1 m^2 glass window, 3.2 mm thick, 20°C inside, and 0°C outside.
Applying Fourier's law:

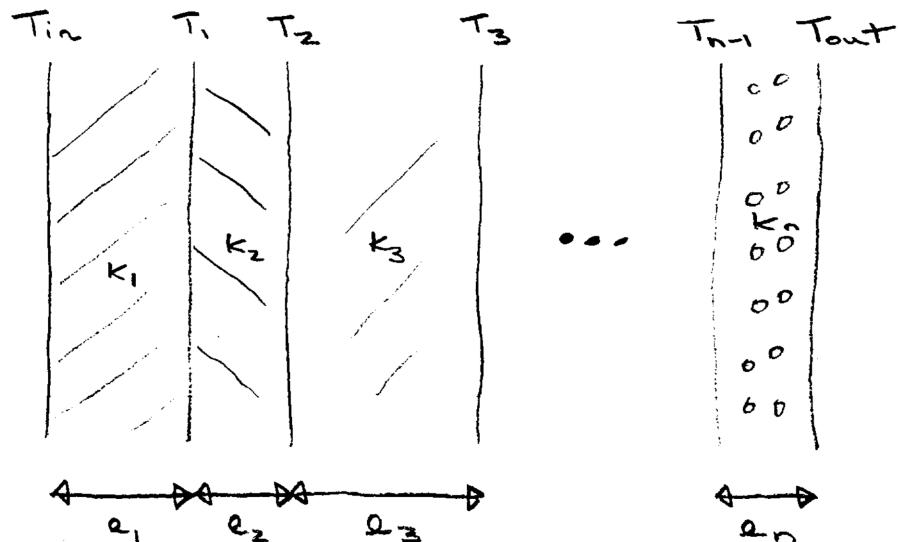
$$\dot{Q}_{\text{in} \rightarrow \text{out}} = -k_t A \frac{T_{\text{out}} - T_{\text{in}}}{\Delta x} \quad (98)$$

$$\approx -0.8 \frac{\text{W}}{\text{m K}} \times 1 \text{ m}^2 \times \frac{-20 \text{ K}}{0.0032 \text{ m}} \quad (99)$$

$$\approx 5000 \text{ W.} \quad (100)$$

In reality, this is an *upper bound* on the heat flow, as there will be a thin boundary layer of air near the glass surface supporting a temperature gradient.

-
- in fact for a “sandwich” of layers:



- in the **steady-state** (i.e., time-independent temperatures) the heat flow across each slab will be equal:

$$\begin{aligned} \frac{\dot{Q}}{A} &= -k_1 \frac{(T_1 - T_{in})}{l_1} \\ \frac{\dot{Q}}{A} &= -k_2 \frac{(T_2 - T_1)}{l_2} \\ &\vdots \\ \frac{\dot{Q}}{A} &= -k_n \frac{(T_{out} - T_{n-1})}{l_n} \end{aligned} \quad \left. \right\} \begin{array}{l} n \text{ layers,} \\ \text{each with the} \\ \text{same heat flow} \end{array} \quad (101)$$

- let us rearrange these equations slightly, to give:

$$\begin{aligned}\frac{\dot{Q}}{A} \frac{\ell_1}{k_1} &= T_{in} - T_1 \\ \frac{\dot{Q}}{A} \frac{\ell_2}{k_2} &= T_1 - T_2 \\ &\vdots \\ \frac{\dot{Q}}{A} \frac{\ell_n}{k_n} &= T_{n-1} - T_{out}\end{aligned}\tag{102}$$

- if we add all of the equations, the intermediate temperatures (T_1, T_2, \dots, T_{n-1}) cancel, yielding:

$$\frac{\dot{Q}}{A} \left(\frac{\ell_1}{k_1} + \frac{\ell_2}{k_2} + \dots + \frac{\ell_n}{k_n} \right) = T_{in} - T_{out}\tag{103}$$

which can be rearranged into a helpful form:

$$\frac{\dot{Q}}{A} = \frac{1}{\left(\frac{\ell_1}{k_1} + \frac{\ell_2}{k_2} + \dots + \frac{\ell_n}{k_n} \right)} (T_{in} - T_{out})\tag{104}$$

The value of ℓ/k_t for a layer is known as its **R-value**. As is apparent from Eq. 104, R-values **add** for layers in series with one another.

- in the SI system, R-values have units of $\frac{\text{K} \cdot \text{m}^2}{\text{W}}$ (following from their definition).
- R-values are often specified for fibreglass insulation to be installed in homes i.e., the pink battens. Unfortunately in this context they are often given without units

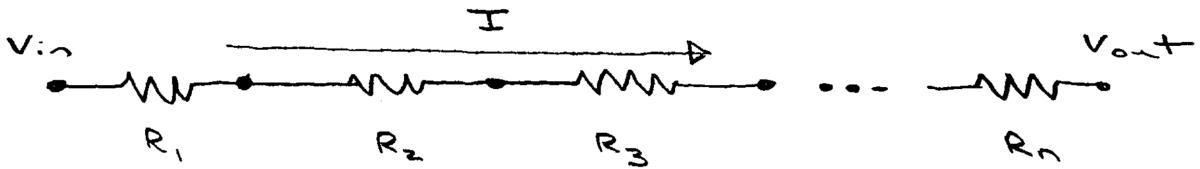
*the archaic "unitless R" has units of
 $\frac{\text{°F} \cdot \text{ft}^2 \cdot \text{hr}}{\text{Btu}}$*

*"British thermal unit"
 energy req'd to raise temperature
 of a pound of water
 by 1° F.*

All hail the metric system!

- incidentally, why the "R" in R-value?

Recall that if we have some resistors in series:



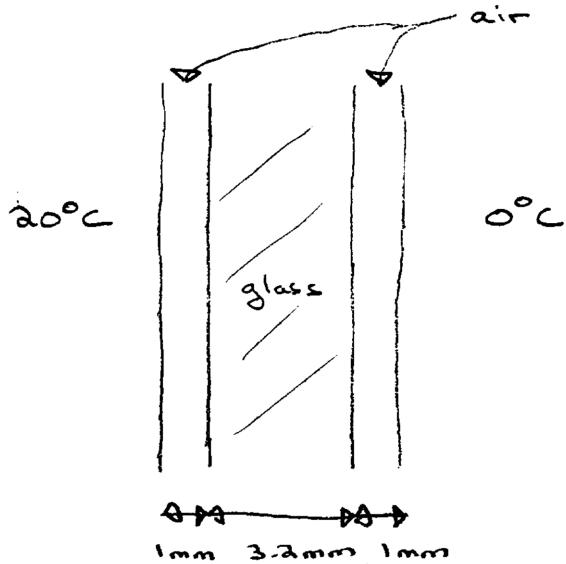
we can compute the current flowing through the resistors as:

$$I = \frac{1}{R_1 + R_2 + \dots + R_n} (V_{\text{in}} - V_{\text{out}}) \quad (105)$$

i.e., the resistances *add* when they are in series.

- notice the similarity between Eq.'s 105 and 104: the Resistances add in the same way that the R -values do. Not too many dots to connect ...
- in fact the derivation of Eq. 105 is essentially the same as that for Eq. 104: we assume that the current through each resistor is the same; similar to the way in deriving Eq. 104 we assumed that the heat from \dot{Q}/A through each layer was the same.
- as a final example, let us consider Problem 1.57d of SITP (paraphrased):

Compute the heat flow through a window that has a still air layer of 1 mm on either side:



Since the layers are “in series” we add their R -values:

$$R_{\text{tot}} = 2R_{\text{air layer}} + R_{\text{window}} \quad (106)$$

$$= \frac{2 \times 10^{-3} \text{ m}}{0.026 \text{ W m}^{-1} \text{ K}^{-1}} + \frac{3.2 \times 10^{-3} \text{ m}}{0.8 \text{ W m}^{-1} \text{ K}^{-1}} \quad (107)$$

$$(108)$$

$$\approx 0.081 \frac{\text{m}^2 \cdot \text{K}}{\text{W}}, \quad (109)$$

and thus:

$$\frac{\dot{Q}_{\text{in} \rightarrow \text{out}}}{A} = \frac{T_{\text{in}} - T_{\text{out}}}{R_{\text{tot}}} \quad (110)$$

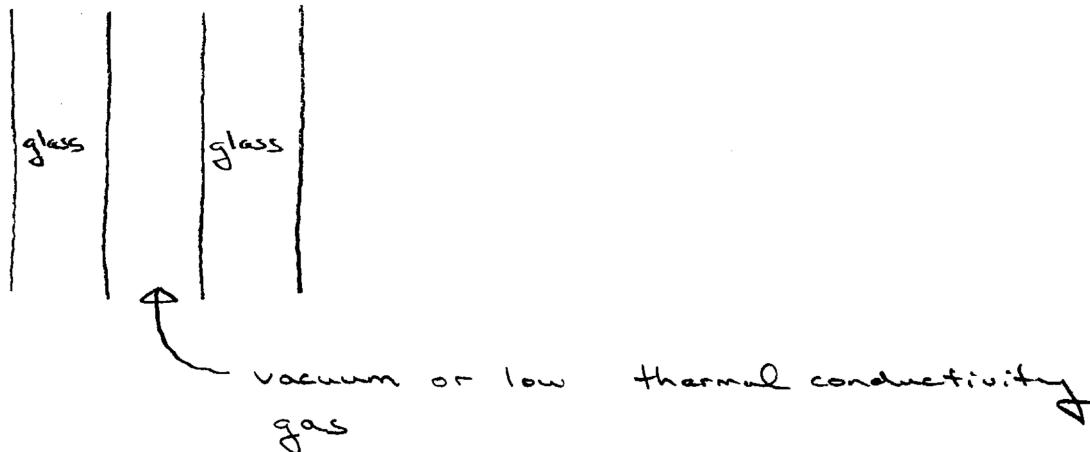
$$= \frac{20 \text{ K}}{0.081 \frac{\text{m}^2 \cdot \text{K}}{\text{W}}} \quad (111)$$

so that finally we have:

$$\boxed{\frac{\dot{Q}_{\text{in} \rightarrow \text{out}}}{A} \approx 250 \frac{\text{W}}{\text{m}^2}} \quad (112)$$

Notice that this much less than the $\approx 5 \text{ kW/m}^2$ value that we computed without the air layers.

- the previous example points to the utility of **doubled-paned glass** or double glazing:



- vacuum is ideal (zero thermal conductivity), but has practical problems (leakage, structural integrity, etc...)
- with air as a filler between the glass, a typical R -value for double glazing is $0.35 \frac{\text{m}^2 \text{K}}{\text{W}}$ (see [wikipedia](#)); contrast to $0.081 \frac{\text{m}^2 \text{K}}{\text{W}}$ in the unglazed example that we have just discussed.

Part II

Entropy and temperature

I am a genius of trivialization.

Lev Landau, as quoted in the [AIP oral history interview with A. Migdal](#).

12 Introduction

- physics abounds with **toy models**: idealizations that retain important qualitative (and possibly quantitative) properties of real physical systems, but yet are easier to analyze. As the Landau quote suggests, the construction of these models is a bit of an art.
- here our goal is to motivate the definitions of entropy S and temperature T . For the same purpose, SITP uses three toy models:
 - (1) the two-state paramagnet,
 - (2) the Einstein solid, and
 - (3) the ideal gas.
- to get to the point a bit more quickly than SITP, we will skip the two-state paramagnet in these notes (deferring treatment to assigned work). We will follow SITP's treatment of the Einstein solid rather closely, but take a slightly more rigorous approach to the ideal gas, reaching similar conclusions.

13 The Einstein solid model

13.1 Introduction to the Einstein solid model (SITP 2.2)

- let us recall a little bit of “spring theory”. For a simple harmonic oscillator with Hamiltonian:

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2, \quad (113)$$

the different energy eigenstates, indexed by $n = 0, 1, \dots$, have energies:

$$E = \hbar\omega \left(n + \frac{1}{2} \right) \quad (114)$$

where $\omega = \sqrt{k/m}$ and \hbar is Planck's constant.

- a solid consisting of a set of N such oscillators, each with the *same* ω , is known as an **Einstein solid**. It provides a crude description of the oscillations of atoms about their equilibrium positions in a solid. For this correspondence to hold true, we should allocate *three* oscillators

per atom (corresponding to each of the three spatial dimensions).³⁸ However, to simplify the expressions in what follows, we will consider the total number of oscillators N as primary (*not* the number of atoms $\approx N/3$).

- later we will see that such a model is in reasonable — but not perfect — agreement with both experiment and more sophisticated models for some solids (Section 13.5 and Problem 3.25 of SITP). We will also touch on the importance of this model in the development of quantum theory (Section 28). However, neither of these points are important for our discussion right now — the Einstein solid is simply a convenient system for introducing some general principles.
- before delving into the details let us make one simplification. Since all of the oscillators are *identical* their $\hbar\omega$ is the same, as is their zero point energy $\hbar\omega/2$. Thus, instead of the energy we will just refer to the integers n_1 , n_2 and so-on as the energy of each of the oscillators, and $n_1 + n_2 + \dots$ for the total energy of all of the oscillators. The bijective correspondence between these integers and the corresponding energies is implicit in what follows.
-  
- to understand entropy and temperature in the Einstein solid, a crucial question is:

Given a total amount of energy q ($:= n_1 + n_2 + \dots + n_N$) for N oscillators, how many different ways may this energy be distributed among the oscillators?

The significance of this question will become clear as we proceed.

- let us start by looking at the answer in for some special cases. For $N = 3$ oscillators:
 1. $q = 0$: there is only one possibility: $n_1 = 0$, $n_2 = 0$, $n_3 = 0$. i.e., none of the oscillators can be excited if the total energy is zero.
 2. $q = 1$: there are three possibilities; the single excitation could possibly be in each of the three oscillators.
 3. $q = 2$: there are six possibilities; two single excitations may be distributed three ways among the oscillators, and one double excitation may be distributed three ways.

³⁸The Hamiltonian in three spatial dimensions: $H = p^2/2m + kr^2/2$ may be written as the sum of three Hamiltonians, each corresponding to a harmonic oscillator in a single dimension: $H = p_x^2/2m + kx^2/2 + p_y^2/2m + ky^2/2 + p_z^2/2m + kz^2/2$. By separation of variables, the total energy of a given three-dimensional oscillator is now the sum of the energies of three independent one-dimensional oscillators, all with the same ω .

In more detail:

$$\begin{aligned}
 q=0 &= n_1 = 0, n_2 = 0, n_3 = 0 & \} \text{ one way} \\
 q=1 &= \begin{cases} n_1 = 1, n_2 = 0, n_3 = 0 \\ n_1 = 0, n_2 = 1, n_3 = 0 \\ n_1 = 0, n_2 = 0, n_3 = 1 \end{cases} & \} \text{ three ways} \\
 q=2 &= \begin{cases} n_1 = 1, n_2 = 1, n_3 = 0 \\ n_1 = 1, n_2 = 0, n_3 = 1 \\ n_1 = 0, n_2 = 1, n_3 = 1 \\ n_1 = 2, n_2 = 0, n_3 = 0 \\ n_1 = 0, n_2 = 2, n_3 = 0 \\ n_1 = 0, n_2 = 0, n_3 = 2 \end{cases} & \} \text{ six ways} \\
 &\text{double excitations} &
 \end{aligned}$$

- what is the general formula? i.e., how many distinguishable ways are there to distribute energy q over N oscillators? Call this $\Omega(N, q)$. By the preceding example: $\Omega(3, 0) = 1$, $\Omega(3, 1) = 3$, and $\Omega(3, 2) = 6$.
- let us use the **stars and bars** method³⁹ to derive the general formula:
 - use q indistinguishable symbols of the form: * to represent excitations, and
 - use $N - 1$ indistinguishable symbols of the form: | to “group” excitations with oscillators.

The number of *distinguishable* ways that the stars and bars can be placed in a line, gives $\Omega(N, q)$. e.g., again for $N = 3$, we have:

$$\begin{aligned}
 q = 1 &: *| | \quad (\text{first oscillator is excited}) \\
 &| *| \quad (\text{second oscillator is excited}) \\
 &| | * \quad (\text{third oscillator is excited})
 \end{aligned}$$

$$\begin{aligned}
 q = 2 &: *| *| \quad (\text{first and second oscillators have single excitation}) \\
 &*| | * \quad (\text{first and third oscillators have single excitation}) \\
 &| *| * \quad (\text{second and third oscillators have single excitation}) \\
 &**| | \quad (\text{first oscillator has double excitation}) \\
 &| **| \quad (\text{second oscillator has double excitation}) \\
 &| | ** \quad (\text{third oscillator has double excitation})
 \end{aligned}$$

When cast in this form, the problem is quite similar to a *much* more familiar one:

What are the coefficients of terms of the form $x^i y^{n-i}$ in the expansion of $(x + y)^n$?

To make the connection to our problem: the coefficient of the $x^i y^{n-i}$ term corresponds to the number of distinguishable ways that i indistinguishable x symbols and $n - i$ indistinguishable

³⁹In previous offerings of Phys 358 some students reported learning about “stars and bars” in their statistics courses.

y symbols may be written out in a line. Think about expanding out $(x + y)^n$ and collecting the like terms. For example, suppose that we had a total of 6 bars and stars:

$$(x + y)^6 = x^6 + 6x^5y + 15x^4y^2 + 20x^3y^3 + 15x^2y^4 + 6xy^5 + y^6. \quad (115)$$

The coefficients on the RHS are the binomial coefficients, and thus:

- there is 1 way to order 6 stars and no bars,
- there are 6 ways to order 5 stars and 1 bar,
- there are 15 ways to order 4 stars and 2 bars,
- there are 20 ways to order 3 stars and 3 bars,
- there are 15 ways to order 2 stars and 4 bars,
- there are 6 ways to order 1 star and 5 bars,
- there is 1 way to order no stars and 6 bars,
- for the general formula, recall the **binomial theorem**:

$$(x + y)^n = \sum_{i=0}^n \binom{n}{i} x^i y^{n-i} \quad (116)$$

where the “choose” symbol is defined as:

$$\binom{n}{i} := \frac{n!}{i!(n-i)!}. \quad (117)$$

With the correspondences:

$$\begin{aligned} i &\rightarrow q \\ n - i &\rightarrow N - 1 \end{aligned}$$

we have, for the Einstein solid:

$\Omega(N, q) = \binom{N - 1 + q}{q}$

(118)

Of course, I have just shifted the burden of proof to the binomial theorem (Eq. 116).

- now let us introduce some terminology in the context of the Einstein model (we will generalize later):
 - q specifies the **macrostate**,
 - the specific distribution of energies among the oscillators is a **microstate**, and
 - the number of microstates contributing to a given macrostate is known as the **multiplicity** of macrostate (we have been using the symbol $\Omega(N, q)$ for the multiplicity of the Einstein solid model).

- different macrostates are expected to be distinguishable at the *macroscopic* level; whereas the microstates corresponding to a given macrostate are expected to be indistinguishable at a microscopic level. The idea is that a given system could “hop” between different microstates corresponding to a given macrostate, without us noticing any change at the microscopic level.
- for now, the distinction between a microstate and a macrostate may seem somewhat artificial and vague. Later, when we discuss similar ideas for the monatomic ideal gas (Section 15) we will consider the pressure, volume, and temperature as macroscopic properties, with many possible combinations for the positions and velocities of the gas molecules (micro-states) contributing to a given macrostate. In this case, the distinction between macro- and micro-states is a bit more clear: we can know the pressure, temperature and volume of a gas (macrostate), but knowing the exact positions and velocities of the constituent molecules (microstate) is unfeasible.

13.2 Two Einstein solids in thermal contact (SITP 2.3)

- this is the toy system that is going to motivate our definition of temperature (finally!).
- an isolated Einstein solid cannot change its macrostate, as that would violate energy conservation.
- however, let us consider *two* Einstein solids, A and B , both with many identical oscillators, but perhaps each with a different number of oscillators.
- if A and B are in thermal contact with each other, but otherwise isolated they can exchange energy as long as the total energy:

$$q := q_A + q_B, \quad (119)$$

remains constant.

- the *pair* of energies, q_A and q_B , now characterize the macrostate (i.e., q_A and q_B are observable on the macroscopic level), and it is possible that the macrostate can change with time.
- for concreteness, let us discuss the same numerical example as SITP (pg.'s 56 and 57): ⁴⁰

solid A has $N_A = 3$ oscillators,
 solid B has $N_B = 3$ oscillators,
 and the total energy is $q = q_A + q_B = 6$.

Tabulating the multiplicities (number of contributing microstates) for each macrostate (cf. Fig. 2.4 of SITP):

⁴⁰The ridiculously small size of this system makes the partitioning into two systems highly artificial, together with the distinction between the macro- and micro-states. In the next section, we will look at more realistic system sizes.

q_A	q_B	Ω_A	Ω_B	$\Omega = \Omega_A \Omega_B$
0	6	1	28	28
1	5	3	21	63
2	4	6	15	90
3	3	10	10	100
4	2	15	6	90
5	1	21	3	63
6	0	28	1	28

Sum is constant,
since total energy is
conserved.

computed using
 $\Omega_B = \binom{N_B - 1 + q_B}{q_B}$

computed using
 $\Omega_A = \binom{N_A - 1 + q_A}{q_A}$

As a check, note that the sum of the multiplicities $\sum \Omega = 28 + 63 + \dots + 63 + 28 = 462$, is consistent with the multiplicity that we would compute by considering the two solids as a single Einstein solid with $N = N_A + N_B = 3 + 3 = 6$ and $q = 6$:

$$\binom{N - 1 + q}{q} = \binom{11}{6} = 462, \quad (120)$$

as expected.

- the tabulation indicates that there are more microstates per macrostate (a larger multiplicity Ω) when the energy is evenly shared between the two solids ($q_A = q_B = 3$). This is important because, to quote SITP (pg. 57), the **fundamental assumption of statistical mechanics** is that:

in an isolated system in thermal equilibrium, all accessible microstates are equally probable.⁴¹

- by this principle, macrostates with large multiplicities are more likely e.g., $q_A = q_B = 3$ with $\Omega = 100$ in our example.
- that the most likely macrostate for two identical Einstein solids is the one for which energy is evenly “shared” seems somewhat intuitive. Nonetheless, for this small system, it is only $100/28 \approx 4$ times more probable than the case where one of the oscillators “hogs” all of the energy ($q_A = 0, q_B = 6$).
- in the next section we will find that as the number of oscillators in each solid is increased, the “sharing” scenario becomes overwhelmingly more probable than the “hogging” scenario.

⁴¹Why should this be true? For our purposes, it is essentially an axiom, with consequences that agree with experimental observations.

13.3 Large system limit (SITP 2.4)

- it is imperative that you understand Stirling's approximation before reading this section. See Appendix E.
- in this section we analyze what happens when the number of oscillators becomes large ($N \approx 10^{23} \approx$ Avogadro's constant) for two Einstein solids in thermal contact.
- we start by deriving an approximate formula for the multiplicity of a single Einstein solid $\Omega(N, q)$, when $q \gg N$. i.e., the number of excitations per oscillator is large. This is not a fundamental restriction, but makes some of the math easier. (To test your skills, try the opposite, $q \ll N$ limit; see Problem 2.17 from SITP, Low-temperature limit of an Einstein solid.)
- starting with the basic exact formula for the multiplicity of a single Einstein solid:

$$\Omega(N, q) = \binom{N - 1 + q}{q} \quad (121)$$

(122)

$$= \frac{(q + N - 1)!}{q!(N - 1)!}. \quad (123)$$

We will ignore difference between N and $N - 1$, so that:

$$\Omega \approx \frac{1}{q!} \frac{(q + N)!}{N!}. \quad (124)$$

Take the “ln” of both sides, giving:

$$\ln \Omega \approx \ln((q + N)!) - \ln(q!) - \ln(N!) \quad (125)$$

and use Stirling's approximation in the form $\ln x! \approx x \ln x - x$ (Eq. 528) so that:

$$\ln \Omega \approx (q + N) \ln(q + N) - (q + N) - q \ln q + q - N \ln N + N \quad (126)$$

$$\approx (q + N) \ln(q + N) - q \ln q - N \ln N \quad (127)$$

Remember that we are interested in the case that $q \gg N$. Here is a common trick technique, based on the Taylor series expansion $\ln(1 + x) \approx x - \frac{1}{2}x^2 + \dots$ (for $|x| \ll 1$):

$$\ln \Omega \approx (q + N) \ln \left(q \left(1 + \frac{N}{q} \right) \right) - q \ln q - N \ln N \quad (128)$$

$$\approx (q + N) [\ln q + \ln(1 + N/q)] - q \ln q - N \ln N \quad (129)$$

$$\approx N \ln q + (q + N) \ln \left(1 + \frac{N}{q} \right) - N \ln N \quad (130)$$

using the Taylor series expansion mentioned above; valid since $|N/q| \ll 1$

$$\ln \Omega \approx N \ln q + (q + N) \frac{N}{q} - N \ln N \quad (131)$$

$$\approx N \ln q + N + N(N/q) - N \ln N \quad (132)$$

and since N/q is small, we neglect the $N(N/q)$ term, and simplify to give:

$$\ln \Omega \approx N \ln \left(\frac{q}{N} \right) + N, \quad (133)$$

or equivalently

$$\Omega = e^{\ln \Omega} \quad (134)$$

$$\approx \left(\frac{q}{N} \right)^N e^N. \quad (135)$$

This approximation to the multiplicity is known as the **high-temperature limit**⁴² of the Einstein solid:

$\Omega \approx \left(\frac{eq}{N} \right)^N \quad \text{for } q \gg N.$

(136)

- now let us use this approximation for two Einstein solids that may exchange energy.
- each solid will have N oscillators and there is a total energy of q to be shared.
- the most probable macrostate has $q_A = q/2$ and $q_B = q/2$; i.e., fair sharing of energy. Let us look at $\Omega_{\text{total}} = \Omega_A \Omega_B$ around this point, using the high-temperature approximation of Eq. 136:

$$\Omega \approx \left(\frac{eq_A}{N} \right)^N \left(\frac{eq_B}{N} \right)^N. \quad (137)$$

- let us measure deviations from the most probable, fair sharing, scenario ($q_A = q_B = q/2$) using $x := q_A - q/2$, so that

$$q_A = q/2 + x \quad \text{and} \quad q_B = q/2 - x. \quad (138)$$

- rewriting the expression for multiplicity (Eq. 137) in terms of x gives:

$$\Omega \approx \left(\frac{e}{N} \right)^{2N} \left(\frac{q}{2} + x \right)^N \left(\frac{q}{2} - x \right)^N \quad (139)$$

$$\approx \left(\frac{e}{N} \right)^{2N} \left[\left(\frac{q}{2} \right)^2 - x^2 \right]^N. \quad (140)$$

Consider approximating the second factor (approximations upon approximations; it is approximations all the way down :)). Take its “ln”:

$$\ln \left(\left[\left(\frac{q}{2} \right)^2 - x^2 \right]^N \right) = N \ln \left(\left(\frac{q}{2} \right)^2 - x^2 \right) \quad (141)$$

$$= N \ln \left[\left(\frac{q}{2} \right)^2 \left(1 - \left(\frac{x}{q/2} \right)^2 \right) \right] \quad (142)$$

$$= N \ln \left(\frac{q}{2} \right)^2 + N \ln \left(1 - \left(\frac{x}{q/2} \right)^2 \right) \quad (143)$$

⁴²At this point it is a bit rich for us to refer to “temperature” of an Einstein solid. Please be patient.

and use $\ln(1 + x) \approx x$ to obtain

$$\approx 2N \ln\left(\frac{q}{2}\right) - N \left(\frac{x}{q/2}\right)^2. \quad (144)$$

- now we substitute this approximation into our expression for Ω (Eq. 140):

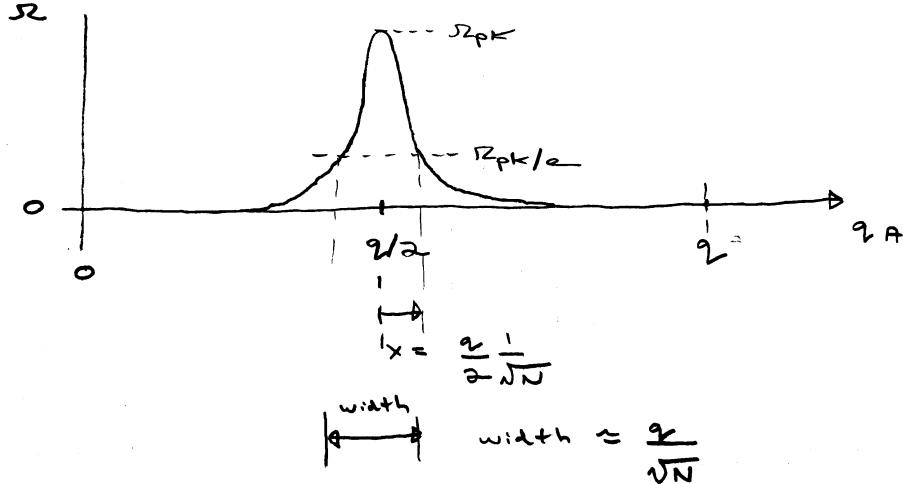
$$\Omega \approx \left(\frac{e}{N}\right)^{2N} e^{2N \ln\left(\frac{q}{2}\right) - N \left(\frac{x}{q/2}\right)^2} \quad (145)$$

$$\approx \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N} e^{-N \left(\frac{x}{q/2}\right)^2} \quad (146)$$

$$\approx \left(\frac{eq}{2N}\right)^{2N} e^{-\left(\frac{x}{q/(2\sqrt{N})}\right)^2} \quad (147)$$

The factor in front is the peak multiplicity, and is consistent with Eq. 137, evaluated with $q_A = q_B = q/2$.

- the multiplicity as a function of deviations x from fair sharing (Eq. 147) is a Gaussian:



- thus we see that the “width” of the energy distribution is a factor of $1/\sqrt{N}$ smaller than the total energy available. e.g., for 1 g worth of material, $N \approx 10^{23}$, and thus energy fluctuations away from energy sharing are a factor $\approx 10^{11}$ less than the energy available for redistribution.
- this small width corresponds to our intuition: in a large system we do not expect it to be probable for 1/2 of the system to “hog” any significant amount of the total energy.
- although we have looked at a specific system as an example, the general idea, namely a $1/\sqrt{N}$ scaling of probable fluctuations away from the most probable scenario, is exhibited by a wide variety of physical systems.
- when fluctuations away from the most probable macrostate are insignificant, we are in what is known as the **thermodynamic limit**.
- a simple Python program to interactively illustrate the development of a Gaussian distribution for q_A as the number of oscillators increases is available here:

<https://gist.github.com/jddmartin/e433f7364c5d757fa5c99ff42ba13fd3>

Here is a video illustrating its use:

<https://web.microsoftstream.com/video/3b8a1669-db9b-45e3-a7ea-4cad13b8a88e>

- for a more intuitive approach to computing the width of the multiplicity function for a system of two large Einstein solids, see SITP Problem 2.22.

13.4 The definition of temperature for Einstein solids 🎥 (SITP 3.1)

- as we have seen, in the system of two Einstein solids (A and B) that can exchange energy, to find the most probable macrostate, we must maximize:

$$\Omega = \Omega_A \Omega_B, \quad (148)$$

where Ω_A is a function of q_A and Ω_B is a function of q_B . However, if we fix the total energy to be q , then $q_B = q - q_A$.

- in this manner, maximizing Ω becomes a problem in single variable calculus. i.e., a necessary condition for a local maxima within an open interval is:



Equivalently:

$$\frac{d}{dq_A}(\Omega_A \Omega_B) = 0. \quad (149)$$

Applying the product rule for derivatives:

$$\left(\frac{d\Omega_A}{dq_A} \right) \Omega_B + \Omega_A \left(\frac{d\Omega_B}{dq_A} \right) = 0. \quad (150)$$

Recall that $q_B = q - q_A$, so that by the chain rule:

$$\left(\frac{d\Omega_B}{dq_A} \right) = - \left(\frac{d\Omega_B}{dq_B} \right). \quad (151)$$

and thus the necessary condition for a maxima (Eq. 149) may be rewritten as:

$$\frac{1}{\Omega_A} \frac{d\Omega_A}{dq_A} = \frac{1}{\Omega_B} \frac{d\Omega_B}{dq_B}. \quad (152)$$

In general, the form:

$$\frac{1}{f} \frac{df(x)}{dx} \quad (153)$$

is known as a **logarithmic derivative**, since

$$\frac{d}{dx} \ln(f(x)) = \frac{1}{f(x)} \frac{d}{dx} f(x). \quad (154)$$

In view of this identity, let us define for every multiplicity, a corresponding **entropy**:

$$S := k \ln \Omega \quad (155)$$

where k is Boltzmann's constant,⁴³ so that Eq. 152 may be written as:

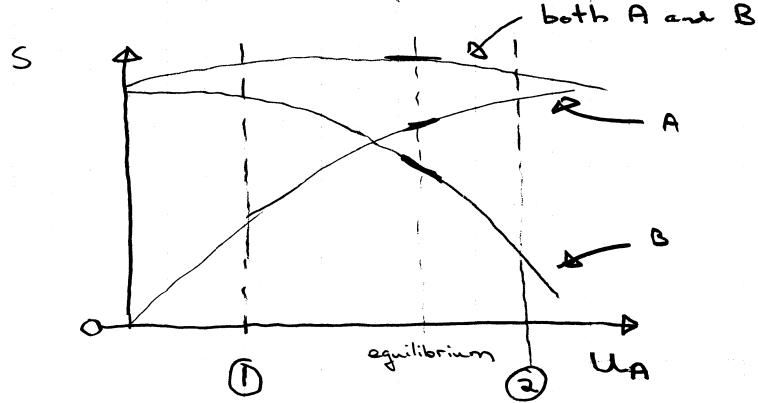
$$\frac{dS_A}{dq_A} = \frac{dS_B}{dq_B}. \quad (156)$$

Since there is a linear relationship between q and the energy of an Einstein solid, we may also write:

$$\frac{dS_A}{dU_A} = \frac{dS_B}{dU_B} \quad (157)$$

for the condition of maximum multiplicity (and entropy) of the two-solid system. i.e., the equilibrium condition.

- let us fix the total system energy U and consider the entropy for each of the two systems and the total system as a function of energy in one system U_A :



- now let us consider three possible conditions indicated on this plot: equilibrium, ①, and ②, but in a slightly strange manner — considering reciprocals — the motivation for which will be obvious shortly:

⁴³The introduction of Boltzmann's constant seems redundant here — and in fact it is a historical accident, not a logical necessity. We will say more about this when we get to the definition of temperature.

at equilibrium : $\frac{1}{dS_A} = \frac{1}{dS_B}$

$$\frac{dS_A}{dU_A} = \frac{dS_B}{dU_B}$$

(1) : $\frac{1}{dS_A} < \frac{1}{dS_B}$

$$\frac{dS_A}{dU_A} > \frac{dS_B}{dU_B}$$

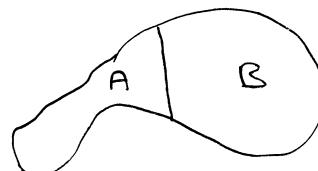
and system A will gain energy and system B will lose energy to achieve equilibrium.

(2) : $\frac{1}{dS_A} > \frac{1}{dS_B}$

$$\frac{dS_A}{dU_A} < \frac{dS_B}{dU_B}$$

and system A will lose energy and system B will gain energy to achieve equilibrium.

Now consider a set of three similar statements about the *temperatures* of two bodies A and B in thermal contact:



at equilibrium : $T_A = T_B$

(1) : $T_A < T_B$

and system A will gain energy and system B will lose energy until $T_A = T_B$

•

(2) : $T_A > T_B$

and system A will lose energy and system B will gain energy until $T_A = T_B$.

- our statements regarding the Einstein solid, where we spoke in terms of

$$\frac{1}{\frac{dS_A}{dU_A}} \quad \text{and} \quad \frac{1}{\frac{dS_B}{dU_B}}$$

and our statements for the generic case of two solids in thermal contact, where we spoke in terms T_A and T_B are *entirely equivalent* if we consider:

$$T_A = \frac{1}{\frac{dS_A}{dU_A}} \quad \text{and} \quad T_B = \frac{1}{\frac{dS_B}{dU_B}} \quad (158)$$

- with this motivation we *define* the temperature of an arbitrary Einstein solid as:

$$T := \frac{1}{\frac{dS}{dU}} \quad (159)$$

or equivalently

$$T := \frac{dU}{dS}. \quad (160)$$

The probabilistic arguments regarding macrostates, microstates, most probable states, etc..., directly correspond to the observed macroscopic heat flow, based on differing temperatures.

- suppose that instead of defining entropy as $S := k \ln \Omega$, we omitted Boltzmann's constant, so that $S := \ln \Omega$. We could then still keep the definition of temperature given in Eq. 160, but now for dimensional consistency, since S is dimensionless, temperature would be measured in the same units as energy; e.g., J. In some sense, measuring temperature in energy units would be more logical. After all, recall that the Kelvin scale is set by the properties of water (≈ 100 K between the melting and boiling points of water). But, as you have no doubt noticed, temperature and energy are horribly conflated in ordinary language. The introduction of units for temperature — different from those of energy — helps clarify that these are distinct physical quantities.

13.5 The heat capacity of the Einstein solid

- in Part I of these notes we just took heat capacities of solids as empirically defined (e.g., ice). We will now test our definition of temperature for the Einstein solid by seeing what heat capacities it predicts.
- recall the high-temperature limit for an Einstein solid (Eq. 136):

$$\Omega \approx \left(\frac{eq}{N}\right)^N \quad (161)$$

for $q \gg N$. Thus the entropy is

$$S = k \ln \Omega \quad (162)$$

$$\approx k \ln \left(\frac{eq}{N}\right)^N \quad (163)$$

$$\approx kN \ln \left(\frac{eq}{N}\right) \quad (164)$$

Recall that from Eq. 114, we have $q = U/(\hbar\omega)$, so that

$$S \approx kN \ln \left(\frac{eU}{Nh\nu} \right) \quad (165)$$

Differentiate wrt U , to obtain

$$\frac{dS}{dU} \approx \frac{kN}{U} \quad (166)$$

and thus by the definition of temperature (Eq. 160):

$$T \approx \frac{U}{kN}. \quad (167)$$

Rearranging gives:

$$U \approx NkT \quad (168)$$

and thus defining heat capacity⁴⁴ as $C := dU/dT$, we have:

$$C \approx Nk. \quad (169)$$

Recall that we started from $\Omega \approx (eq/N)^N$, a valid approximation when $q \gg N$, or equivalently $U/(h\nu) \gg N$ i.e., on average, many quanta per oscillator. Since high- U corresponds to high- T , we say call $q \gg N$ the **high- T** regime. Problem 3.25 of SITP (important), asks you to consider C for general T , including the low- T regime.

- does the high- T result (Eq. 169) have any correspondence to reality? Yes! Recall that from our [introductory discussion](#) of the Einstein solid, we mentioned that we should assign *three* oscillators per atom, so that:

$$N = 3N_{\text{atoms}} \quad (170)$$

$$= 3N_A n, \quad (171)$$

where N_A is the Avogadro constant, and n is the number of moles of atoms. Thus the molar specific heat capacity is

$$\frac{C}{n} \approx 3N_A k, \quad (172)$$

or using the ideal gas constant $R = N_A k$:

$$\frac{C}{n} \approx 3R \quad (173)$$

a result known as the **Dulong-Petit law**. See the plot at the [wikipedia page](#) comparing the heat capacities of a variety of elements at room temperature. Of course, to reliably apply the Dulong-Petit law we need to know if we are in the high- T regime.

⁴⁴ The Einstein model has no notion of volume or pressure, so C is neither C_V or C_P . Recall that for ideal gases $C_P - C_V = Nk$, so that a theory predicting heat capacities of order Nk that does not distinguish between C_P and C_V seems worthless. However, for solids and liquids, the differences between C_P and C_V are often less pronounced than for gases. For example, [SITP Problem 5.14](#) shows that for water at room temperature, $(C_P - C_V)/C_P \approx 0.01$. By contrast, for a noble gas at room temperature $(C_P - C_V)/C_P \approx 0.4$.

- remember that the actual “fidelity” of the Einstein model to physical reality is not our primary concern here — this toy model is just a vehicle for introducing micro- and macro-states, multiplicity, entropy and a definition of temperature. With that caveat, some final points may be of interest to you (but are *not* “required knowledge”):
 - Figure 7.29 of SITP (pg 312) illustrates that the more sophisticated “Debye model” also gives the same high- T result for C as the Einstein model. The Debye model is an improvement over the Einstein model at low- and intermediate- T .
 - in the language of Appendix C — which discusses the equipartition theorem and my apathy towards it — the high- T limit “unlocks” vibrations. In fact, Eq. 169 corresponds to the equipartition theorem with $f = 2$, which we might expect based on the Hamiltonian $H = p_x^2/2m + \frac{1}{2}kx^2$ (i.e., “two-quadratic-like degrees of freedom contributing to the energy”). In Appendix C I discuss the classical nature of the equipartition theorem. That is consistent with the absence of Planck’s constant \hbar from Eq. 169. However, the low- T behaviour of both the Einstein and Debye models and their transition to the high- T classical behaviour is as “quantum” as it gets.

14 Two-state systems (SITP 2.1, 3.3)

- the Einstein model has no concept of volume or pressure. Another model system that also has no sense of volume is the so-called **two-state system**: in contrast to the Einstein model, where each of the N sites is one of an *infinite* number of states that correspond energies $\frac{1}{2}\hbar\omega$, $\frac{3}{2}\hbar\omega$, $\frac{5}{2}\hbar\omega$, …, instead we consider that each one of N sites is in one of *two* states, either of energy 0 or ϵ .
- the canonical instance of the two-state system is a set of N spin-1/2 systems in a magnetic field. Each spin has a magnetic moment of μ and thus an energy of μB or $-\mu B$ depending on its orientation in the magnetic field B . Here $\epsilon = 2\mu B$. SITP phrases the conversation of two-systems around these **two-state paramagnet** systems, but they are just one physical manifestation of the two-state model.
- the two-state system illustrates an important point: temperature is not always easily associated with a “random motion” of some sort, as frequently done in qualitative accounts. The association is straightforward for an ideal gas, and also for the Einstein model of a solid (as each oscillator has a motion associated with it). However, this description is rather strained for two-state systems: in the case of the magnetic dipole, are we to consider the flipping of the dipole to be a motion of sorts? No! It is the relation between entropy and temperature that dictates temperature. As long as we can identify the macro and micro-states and count multiplicities, we can identify a relationship between energy and temperature (and possibly other variables, such as pressure and volume, as we will discuss in the next section).
- the same process that we used to determine the energy - temperature relationship for the Einstein solid may be used for the two-state system:

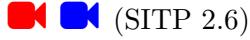
model → Ω → S → T → C → comparison with “reality”.

For an example, see “Shocking Schottky” in the [extended example problems](#).

This same procedure is applicable to any model without a notion of volume or pressure.⁴⁵

15 Monatomic ideal gases

15.1 The entropy of monatomic ideal gases (Sackur-Tetrode equation)



- we now consider the multiplicity, entropy, and temperature for an ideal gas. The main point of interest is the generalization of $T := dU/dS$, as was applied to the Einstein solid and two-state paramagnet, which have no sense of volume (or pressure), to $T := (\partial U/\partial S)_V$.
- SITP uses a mixture of classical and quantum mechanics to arrive at an expression for Ω for an ideal gas. A slightly different, more “quantum” approach will be taken here.⁴⁶
- recall one of the “baby problems” of quantum mechanics: a single particle of mass m confined within an infinite one-dimensional square well of width L . Its energy levels are given by⁴⁷

$$E = \frac{1}{2m} \left(\frac{\hbar\pi}{L} \right)^2 n^2 \quad (174)$$

with $n = 1, 2, 3, \dots$

- a straightforward generalization is to a particle confined to cubic box of dimensions $L \times L \times L$ in three spatial dimensions:

$$E = \frac{1}{2m} \left(\frac{\hbar\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2) \quad (175)$$

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

- we are interested in N non-interacting particles so that the total energy of a given microstate is:

$$\begin{aligned} U = & \frac{1}{2m} \left(\frac{\hbar\pi}{L} \right)^2 (n_{1x}^2 + n_{1y}^2 + n_{1z}^2 + \\ & n_{2x}^2 + n_{2y}^2 + n_{2z}^2 + \\ & \dots \\ & n_{Nx}^2 + n_{Ny}^2 + n_{Nz}^2) \end{aligned} \quad (176)$$

with the microstate characterized by $n_{1x}, n_{1y}, \dots, n_{Nz}$.

⁴⁵As noted in the [concluding remarks](#) for this Part, the approach that we are using here — counting multiplicities for a fixed system energy — will be replaced by a more efficient procedure in Phys 359, *Statistical Mechanics*.

⁴⁶The discussion here is based on R. K. Pathria and P. D. Beale, *Statistical mechanics*, 3rd ed (Elsevier/Academic Press, Amsterdam ; Boston, 2011).

⁴⁷A particle confined to an infinite square well is treated in many introductions to quantum mechanics. See, for example, “The particle in a box” in Appendix A of SITP, pages 368–369.

- we now have the same task that we had for the Einstein solid and two-state paramagnet, namely determining the multiplicity of the macrostates:

Given a U (specifying a macrostate), how many different distinct tuples of positive integers $n_{1x}, n_{1y}, \dots, n_{Nz}$, (microstates) satisfy Eq. 176?

There is no known explicit function for Ω given U . We need a different approach.

- let us temporarily drop into two spatial dimensions and consider only a single particle, enabling us to visualize the difficulty with counting. Specifically, given E , how many positive integers n_x, n_y can satisfy

$$E = \frac{1}{2m} \left(\frac{\hbar\pi}{L} \right)^2 (n_x^2 + n_y^2) \quad (177)$$

Let us define a “radius” $R := \sqrt{2mE} \times L / (\hbar\pi)$, so that we may view the problem geometrically: given a circle radius R , how many points lie on its circumference, where the “points” correspond to different quantum states?

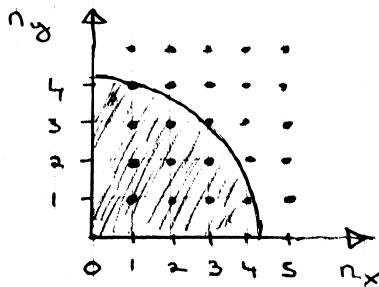


Figure 17: Counting the states for a single particle in two spatial dimensions. The value of $N_<(E)$ is given by the number of “dots” within the quarter-circle of radius $R = \sqrt{2mE} \times L / (\hbar\pi)$.

Obviously, depending on their radii, many circles will have *no* states on their circumference. For those circles that do have states on their circumference, counting how many seems rather difficult.

However instead of direct counting, we may turn the problem into one amenable to the continuous variable toolbox.⁴⁸

Specifically, instead of directly counting how many points lie on a circle of a given radius, we shall instead estimate how many points lie *within* the circle,⁴⁹ i.e., how many pairs of positive integers, n_x and n_y , satisfy $n_x^2 + n_y^2 < R^2$? Call this $N_<(E)$.⁵⁰ Obviously we will need to explain how solving this different problem solves the original problem. But for now, let us assume that we will be able to make that connection.

⁴⁸Not a big deal — we were going to have to make the transition to continuous variables at some point (to take derivatives to obtain the relationship between energy and temperature. The difference is that for the Einstein solid and two-state paramagnet we did this later in the process with the introduction of Stirling’s approximation.

⁴⁹Counting the number of lattice points within a circle of arbitrary radius is essentially the [Gauss circle problem](#), for which no exact solution is known.

⁵⁰We might have a vague notion that somehow we might be able to “differentiate” $N_<(E)$ wrt E to determine Ω . However, how we might accomplish this — or at least a version of it — is deferred until after we have determined $N_<(U)$ for a system of N particles.

- the “density” of quantum states in our hypothetical space is 1 (there is one “dot” per square in Fig. 17). So we may *estimate* $N_<(E)$ by multiplying this density by the area of a quarter circle of radius R :

$$N_<(E) = \frac{1}{4}\pi R^2. \quad (178)$$

The factor of 1/4 accounts for the fact that we are only interested in states which lie in a particular **quadrant** of the plane — the one corresponding to positive n_x and n_y .

As R increases, the difference between “exact counting” of the states within R and the approximation given by Eq. 178 becomes insignificant (as a fraction):

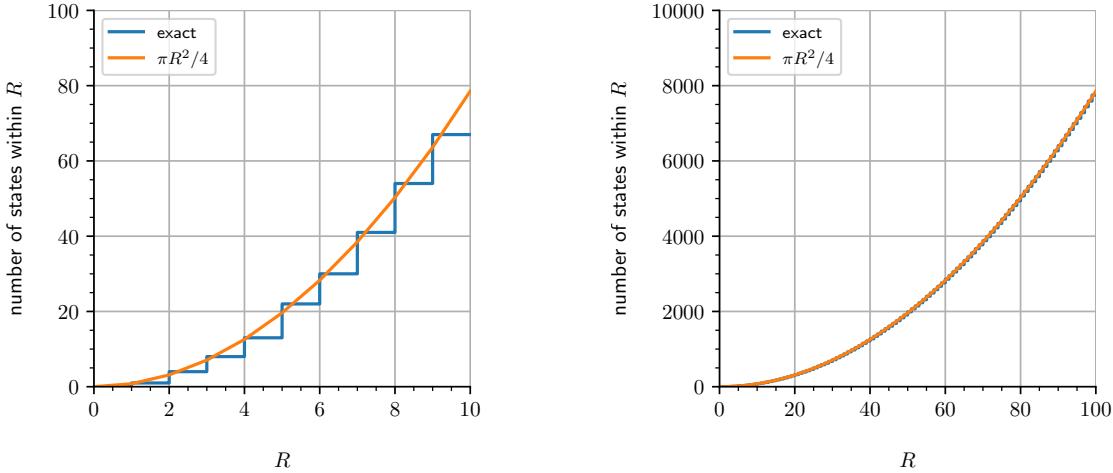


Figure 18: Exact counting and approximate counting (Eq. 178) of the number of states within R over two different ranges in R .

- moving from a single particle in two spatial dimensions to one in *three* dimensions — with energy given by Eq. 175 — we now define a similar “radius” $R := \sqrt{2mE} \times L/(\hbar\pi)$, and estimate many states are within a *sphere* of that radius, by:

$$N_<(E) = \frac{1}{8} \frac{4\pi}{3} R^3. \quad (179)$$

Why the 1/8 factor? Because we are only interested in the volume of an *octant* of the sphere — the octant corresponding to positive values of n_x , n_y and n_z (instead of a quadrant in the case of two dimensions giving a 1/4 factor).

- now we generalize the preceding results for a single particle in two and three spatial dimensions to an arbitrary number of particles N of total energy U in three spatial dimensions:

$$N_<(U) = \frac{1}{2^{3N}} V_{3N}(R), \quad (180)$$

where $V_{3N}(R)$ is the volume of a **hypersphere** of radius $R := \sqrt{2mU} \times L/(\hbar\pi)$ in a space of dimension $d = 3N$ (the number of terms in Eq. 176), and again the $1/2^{3N}$ factor accounts for our interest in all positive $n_{1x}, n_{1y}, \dots, n_{Nz}$ (there are $3N$ of these quantum numbers).

- a derivation of the volume of a hypersphere in arbitrary spatial dimensions may be found in Appendix F. The result is

$$V_d(R) = \frac{\pi^{d/2}}{\Gamma\left(\frac{d}{2} + 1\right)} R^d, \quad (181)$$

where the **gamma function** $\Gamma(x)$ is an “extension” of the factorial function to the reals, i.e., $\Gamma(x) = (x - 1)!$ for positive integer x (see Appendix E). However, since we intend to use Stirling’s approximation — which is equally valid for the gamma function — we will simply write $\Gamma\left(\frac{d}{2} + 1\right)$ as $(d/2)!$.

- using our expression for the volume of the hypersphere, Eq. 181, in Eq. 180, gives

$$N_<(U) = \frac{1}{2^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} \left[\frac{U}{\frac{1}{2m} \left(\frac{\hbar\pi}{L} \right)^2} \right]^{3N/2}. \quad (182)$$

Replacing \hbar by $h/(2\pi)$ and simplifying a bit gives:

$$N_<(U) = \frac{\pi^{3N/2}}{(3N/2)!} \frac{V^N}{h^{3N}} (2mU)^{3N/2} \quad (183)$$

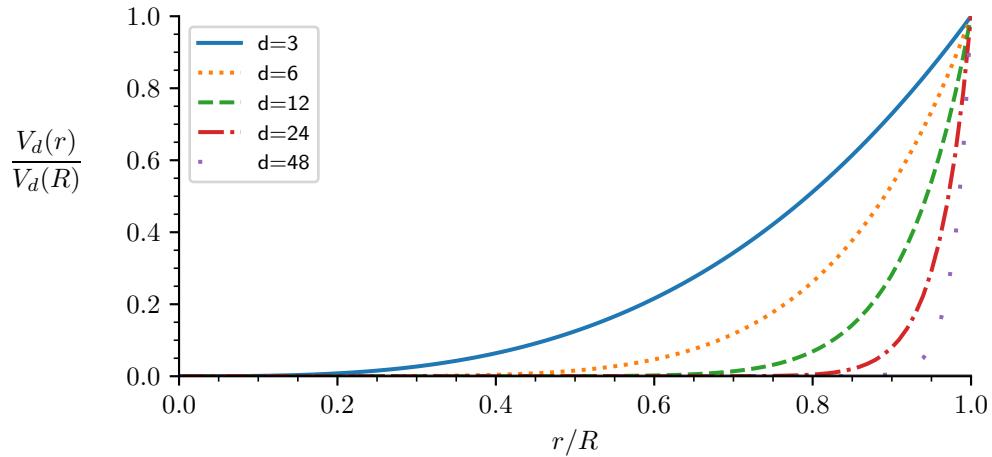
where L^3 has been replaced by the volume V in which the particles are confined to (that is *not* the volume of the hypersphere).

- now we must make the connection between $N_<(U)$ and what we are actually interested in: Ω as a function of U . Differentiating $N_<(U)$ with respect to U gives us a **density of states** $dN_<(U)/dU$. However, to get an Ω , we need some sort of range of energies ΔU , so that

$$\Omega \approx \frac{dN_<(U)}{dU} \Delta U. \quad (184)$$

What should this ΔU be?

- some insight into the answer may be gained by considering how the volume of a hypersphere grows with its radius for different dimensions d .



where I have used $V_d(r)/V_d(R) = (r/R)^d$, as apparent from Eq. 181.

We see that as d increases, the contribution to volume of a hypersphere becomes more and more concentrated at the surface of the hypersphere $r \approx R$. The inner core of the hypersphere contributes less and less to the volume as a fraction of the total. Since in our problem, the dimensionality of the hypersphere is exceedingly large i.e., $d = 3N$, we expect that at a given energy U , the vast majority of microstates contributing to $N_<$ are of an energy close enough to U so that we might as well just say that $\Omega = N_<(U)$ (in effect $\Delta U \approx U$). Admittedly that's a bit tough to accept — but higher dimensional spaces are quite non-intuitive. (The choice of $\Omega = N_<(U)$ may be rigorously justified by considering the N dependence of the entropy when this approximation is *not* made.⁵¹)

- there is a final important subtlety to consider relating the distinguishability — or lack thereof — of the particles. If the atoms of the gas are truly indistinguishable then Ω *overcounts* the number of states. As a simplified example of this overcounting, consider a two-atom system, in one dimension, so that each microstate is characterized by n_{1x} and n_{2x} . If the two atoms are truly indistinguishable then the microstate: $n_{1x} = 1, n_{2x} = 2$ is indistinguishable from the microstate: $n_{1x} = 2, n_{2x} = 1$ and thus should not be counted twice. Provided none of the atoms in a given microstate are in the same state (e.g. $n_{1x} = 1, n_{2x} = 1$ for our simple example), then we will have over-counted by a factor of $N!$, and so may simply divide Ω by $N!$ to correct for this over-counting. Double, triple, etc... occupancy becomes more and more rare the hotter and more dilute a gas becomes.⁵²
- so finally, with $\Omega = N_<(U)/N!$, we have:

$$\Omega_N \approx \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} (\sqrt{2mU})^{3N}. \quad (\text{Eq. 2.40 of SITP})$$

⁵¹See R. K. Pathria and P. D. Beale, *Statistical mechanics*, 3rd ed (Elsevier/Academic Press, Amsterdam ; Boston, 2011).

⁵²When the particles are bosons, entering the regime where this approximation (the neglect of higher occupancies) is violated corresponds to the phenomena of **Bose-Einstein condensation**, a subject that we will completely neglect in this course, but which you will discuss in Phys 359.

to which one may apply Stirling's approximation to obtain the **Sackur-Tetrode** equation:

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]. \quad (\text{Eq. 2.49 of SITP})$$

Note that the m that appears here is *not* the mass of the total collection of atoms, but rather, the mass of a single atom, as apparent from its introduction in Eq. 174. It is a good exercise to show that the entropy given by the Sackur-Tetrode equation is *extensive*.

It will be useful in what follows, to define the **thermal de Broglie wavelength**.⁵³

$$\lambda := \left(\frac{4\pi mU}{3Nh^2} \right)^{-1/2}, \quad (185)$$

so that the Sackur-Tetrode equation may be written as:⁵⁴

$$S = Nk \left[\ln \left(\frac{V}{N} \frac{1}{\lambda^3} \right) + \frac{5}{2} \right] \quad (186)$$

The condition $V/N \gg \lambda^3$, is precisely that for the validity of neglecting double, triple, etc... occupancies of states — as discussed above in the derivation of the Sackur-Tetrode equation. Said in another (approximate) way: for the gas to be *classical*, we require that the average separation of the atoms $(V/N)^{1/3}$ be significantly greater than the thermal de Broglie wavelength λ . (This comparison between separations and the de Broglie wavelength is often made in accounts of Bose-Einstein condensation for laypersons.)

-
- if we differentiate the Sackur-Tetrode equation wrt U , while holding V constant we obtain:

$$\left(\frac{\partial S}{\partial U} \right)_V = Nk \frac{d}{dU} (\ln U^{3/2}) \quad (187)$$

$$= \frac{3}{2} Nk \frac{1}{U}. \quad (188)$$

Thus, if $T := (\partial U / \partial S)_V$ (to be justified in the next section) then for the monatomic ideal gas:

$$T = \frac{1}{\frac{3}{2} Nk \frac{1}{U}}. \quad (189)$$

Equivalently,

$$U = \frac{3}{2} Nk T \quad (190)$$

⁵³In Section 5 we computed the average kinetic energy of an ideal gas molecule $\langle KE \rangle = (3/2)kT$. If from that we compute a corresponding speed $v \approx \sqrt{2 \langle KE \rangle / m}$, then apart from a constant factor, the thermal de Broglie wavelength is $\lambda = h/(mv)$.

⁵⁴In SITP, instead of λ Schroeder uses $V_Q := \lambda^3$ — a so-called “Quantum volume”. Usage of λ is a bit more common, so I prefer to use it in these notes. A slightly more convenient form for λ than Eq. 185 is given in Eq. 191.

which is consistent with what we expect for monatomic gases, based on the discussion in Section 5, namely that $C_V = (3/2)Nk$. (See temperature independent heat capacities of the noble gases as illustrated in Fig. 5.)

- revisiting Fig. 5 of Section 5, gives me an opportunity to accentuate the point that Sackur-Tetrode equation does not apply to *all* ideal gases — only monatomic ones. More specifically, the Ω 's for dilute gases of *molecules* are not given by Eq. 2.40 of SITP, but instead must account for the additional possibilities associated with their different possible internal states (of rotation and vibration).⁵⁵ The systematic treatment of the heat capacities of molecules is, yet again, the domain of statistical mechanics (Phys 359); see the [closing words](#) for this Part.
- knowing that $U = \frac{3}{2}NkT$ for a monatomic ideal gas allows us to rewrite the thermal de Broglie wavelength (defined by Eq. 185) in a slightly more convenient form:⁵⁶

$$\lambda := \sqrt{\frac{2\pi\hbar^2}{mkT}} \quad (191)$$

15.2 The general definition of temperature

- recall that for a quasi-static process, the first law gives:

$$dU = Q - PdV + \text{other forms of work}. \quad (192)$$

Recall that Q is the flow of energy into the system, that can't be accounted for as type of work being done on the system. We will now say more about Q .

- if we write the energy U of a system as a function⁵⁷ of S, V, \dots , then:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV + \dots \quad (193)$$

In our discussion of interacting solids, we were able to discuss the approach to thermal equilibrium by the exchange of energy, without any work being done — recall that the Einstein solid

⁵⁵Accounting for internal states is also sometimes necessary for monatomic gases, but not the noble gases. To be more precise: as we have written the Sackur-Tetrode equation, it applies to monatomic ideal gases that can be considered to have *no internal degrees of freedom*. Some of the non-noble monatomic gases have low lying states that do not permit this simplified view, the specifics depending on the temperature. But since these atoms are frequently found in molecular form — unlike the noble gases — naive use of the Sackur-Tetrode equation for them is rarely correct anyways.

⁵⁶It is useful to note that $\lambda \approx 1.0 \times 10^{-10}$ m for hydrogen atoms at 300 K. Wavelengths for other species and temperatures can readily be obtained from the $1/\sqrt{mT}$ scaling of Eq. 191. Since the “size” of a hydrogen atom is about 10^{-10} m, this numerical value of λ makes it clear that Bose-Einstein condensation $V/N \lesssim \lambda^3$ involves a combination of low temperatures and high densities that are atypical for gases.

⁵⁷That we may write $U(S, V, \dots)$ is sometimes taken as an axiom of classical thermodynamics e.g., H. B. Callen, *Thermodynamics and an introduction to thermostatics*, 2nd ed (Wiley, New York, 1985). I am deliberately being (annoyingly) vague about the other variables, for now. These are variables, known as **general displacements** which if held constant, are such that no work can be done. An important addition to this set of variables, relevant when the number and type of particles in a system may change, takes place in Section 16.4, where the “chemical potential” is introduced.

model has no concept of volume or pressure. For the Einstein solid, we defined $T := dU/dS$. Comparison of Eq. 192 with 193 suggests that we now generalize our definition of temperature to:

$$T := \left(\frac{\partial U}{\partial S} \right)_{\text{no work}} \quad (194)$$

where “no work”, means: take the derivative holding V , and any other “generalized displacements” constant so that no work is done “as the system changes”. Like in the case of the Einstein solid, if we know S in terms of U, V, \dots , the equivalent form: $1/T = (\partial S/\partial U)_{\text{no work}}$ may be more convenient.

- we now have an expression for Q for *quasi-static processes*:⁵⁸ $Q = TdS$, so that

$$dU = TdS + \left(\frac{\partial U}{\partial V} \right)_S dV + \dots, \quad (195)$$

and we also surmise that

$$P = - \left(\frac{\partial U}{\partial V} \right)_{S,\dots}. \quad (196)$$

Or equivalently, by the triple-product rule (see Appendix A)⁵⁹:

$$P = \left(\frac{\partial U}{\partial S} \right)_V \left(\frac{\partial S}{\partial V} \right)_U \quad (197)$$

$$\boxed{P = T \left(\frac{\partial S}{\partial V} \right)_U} \quad (198)$$

- let us test this expression for P in the ideal gas case. From the Sackur-Tetrode expression for S for a monatomic ideal gas (Eq. 2.49 of SITP), we obtain:

$$\left(\frac{\partial S}{\partial V} \right)_U = Nk \frac{d}{dV} \ln V \quad (199)$$

$$= \frac{Nk}{V}, \quad (200)$$

so that by Eq. 198

$$P = \frac{T N k}{V}. \quad (201)$$

i.e., the ideal gas law.

- we never explicitly used the ideal gas law in our “derivation” of the Sackur-Tetrode equation. In a limited sense, we have “derived” the ideal gas law (at least for a monatomic gas with no internal degrees of freedom).

Equation 198 provides a means to determine equations of state, not just for the ideal gas — as we have shown — but generally, provided we have S as a function of U and V .

⁵⁸Actually, for $Q = TdS$ to be valid, the system has to be changing in such a way that all work terms involving the general displacements, contribute to the total work W . This point, which is crucial for chemical reactions, is elaborated on in Section 16.4.

⁵⁹It is a bit awkward to explicitly indicate, but all generalized displacements, other than V , are being held constant in Eq.’s 197 and 198.

15.3 Another check of the Sackur-Tetrode equation

- consider an ideal gas with a temperature-independent C_V undergoing quasi-static adiabatic compression/expansion. Recall, from Section 8.3, that:

$$\frac{P_f}{P_i} = \left(\frac{V_i}{V_f} \right)^\gamma. \quad (202)$$

Equivalently:

$$\frac{T_f}{T_i} = \left(\frac{V_i}{V_f} \right)^{\gamma-1}. \quad (203)$$

For a *monatomic* ideal gas, we also have $U = \frac{3}{2}NkT$ and $\gamma - 1 = 2/3$, so that:

$$\frac{U_f}{U_i} = \left(\frac{V_i}{V_f} \right)^{2/3}. \quad (204)$$

Rearranging gives:

$$U_f^{3/2}V_f = U_i^{3/2}V_i, \quad (205)$$

so that under quasi-static adiabatic expansion/compression of a *monatomic* ideal gas, we should consider the value of $U^{3/2}V$ to be a constant.

- now recall the Sackur-Tetrode equation (Eq. 2.49 of SITP), which also applies to a monatomic ideal gas:

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]. \quad (206)$$

Observe that if $U^{3/2}V$ = a constant, then entropy is also constant.

- thus we are lead to conclude that for quasi-static, adiabatic expansion/compression of a monatomic ideal gas, its entropy remains constant. This conclusion is entirely consistent with

$$dU = TdS - PdV. \quad (207)$$

i.e., for $Q = 0$, $dS = 0$, and thus this quasi-static, adiabatic process is **isentropic** (maintains constant entropy).

- for example, in the speed of sound equation (see, for example, Problem 1.39 of SITP):

$$c_s = \sqrt{\frac{B}{\rho}} \quad (208)$$

we should normally use the *isentropic* bulk modulus:

$$B_S := -V \left(\frac{\partial P}{\partial V} \right)_S \quad (209)$$

corresponding to compression and expansion with no heat flow, instead of the isothermal bulk modulus:

$$B_T := -V \left(\frac{\partial P}{\partial V} \right)_T \quad (210)$$

(to avoid Newton's [mistake](#)).

16 The 2nd law of thermodynamics

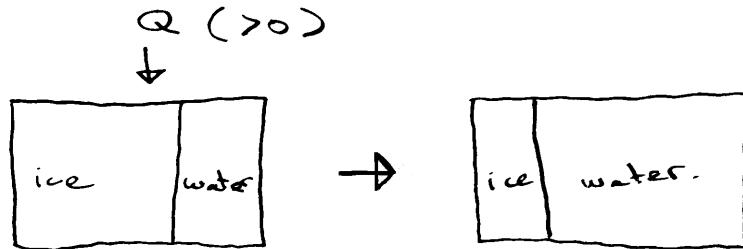
A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.

Albert Einstein

16.1 The relationship between entropy and heat flow

- what are the implications of $Q = TdS$?

e.g., when we add heat to a system to melt ice into liquid water:



$$\Delta S_{\text{ice-water mixture}} = \frac{Q}{T} \quad (211)$$

where $Q = Lm$, where $L \approx 333 \text{ J/g}$ for melting at 1 bar. Thus the entropy of the ice-water mixture *increases* as the ice melts, even though the temperature of the mixture remains the same 0 °C.

- that the entropy of water is greater than ice seems to make sense. i.e., more microstates, more possibilities for the liquid vs. solid.
- now let us consider what happens to the total entropy of two systems, each at a different temperature, when heat flows from the hot to the cold system (without an appreciable change in temperature of either):

$$\Delta S_{\text{tot}} = \Delta S_H + \Delta S_C \quad (212)$$

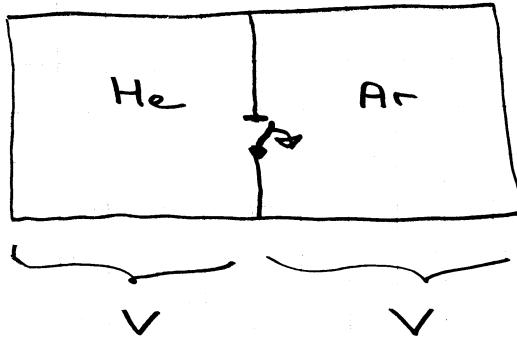
$$= -\frac{Q}{T_H} + \frac{Q}{T_C} \quad (213)$$

$$= Q \left(\frac{1}{T_C} - \frac{1}{T_H} \right), \quad (214)$$

and thus $\Delta S_{\text{tot}} > 0$ for $T_H > T_C$. In other words, total entropy increases when heat flows from hot to cold.

16.2 The entropy of mixing (SITP pages 79-81)

- suppose that we have two types of gas, He and Ar, in two separate chambers, and open a door allowing them to mix:



There are N atoms of He and N atoms of Ar.

To compute the change in entropy we use Eq. 186:

$$\Delta S_{\text{He}} = S_{\text{He, after}} - S_{\text{He, before}} \quad (215)$$

$$= Nk \left[\ln \left(\frac{2V}{N} \frac{1}{\lambda^3} \right) + \frac{5}{2} \right] - Nk \left[\ln \left(\frac{V}{N} \frac{1}{\lambda^3} \right) + \frac{5}{2} \right] \quad (216)$$

$$= Nk \ln 2. \quad (217)$$

Likewise for argon, so that

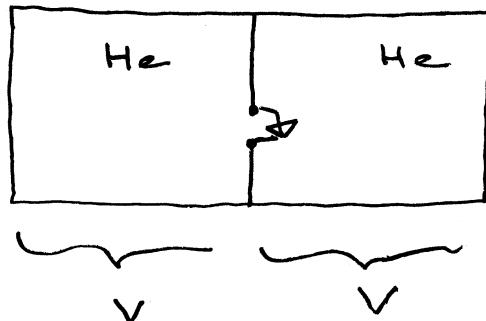
$$\Delta S_{\text{tot}} = \Delta S_{\text{He}} + \Delta S_{\text{Ar}} \quad (218)$$

$$= 2Nk \ln 2. \quad (219)$$

$$(220)$$

Entropy increases upon mixing, which is what we might expect based on any vague preconceptions that we might have regarding entropy. Once mixed, it is certainly unlikely that the two gases would “unmix”.

- now let us imagine:



Each container has N atoms of He, so that $N_{\text{tot}} = 2N$. Also, $V_{\text{tot}} = 2V$.

Upon opening the door:

$$\Delta S = S_{\text{after}} - S_{\text{before}} \quad (221)$$

$$= N_{\text{tot}}k \left[\ln \left(\frac{V_{\text{tot}}}{N_{\text{tot}}} \frac{1}{\lambda^3} \right) + \frac{5}{2} \right] - 2Nk \left[\ln \left(\frac{V}{N} \frac{1}{\lambda^3} \right) + \frac{5}{2} \right] \quad (222)$$

$$= 2Nk \left[\ln \left(\frac{2V}{2N} \frac{1}{\lambda^3} \right) + \frac{5}{2} \right] - 2Nk \left[\ln \left(\frac{V}{N} \frac{1}{\lambda^3} \right) + \frac{5}{2} \right] \quad (223)$$

$$= 0 \quad (224)$$

which makes sense. i.e., what is the difference between before and after?

- however, there is an interesting point to be made here, relating to our derivation of the Sackur-Tetrode equation: The $1/N!$ factor in the multiplicity Ω ([Eq. 2.40 of SITP](#)) accounted for the indistinguishability of the particles. Suppose that this factor was not present. Then instead of Sackur-Tetrode, we would have:⁶⁰

$$S = Nk \left[\ln \left(\frac{V}{\lambda^3} \right) + \frac{3}{2} \right] \quad (\text{wrong}). \quad (225)$$

Note no $1/N$ factor in the argument of \ln and $3/2$ instead of $5/2$.

- now let's recompute the entropy change associated with mixing of two chambers of He gas, using this wrong version of Sackur-Tetrode:

$$\Delta S_{\text{tot}} = S_{\text{after}} - S_{\text{before}} \quad (226)$$

$$= N_{\text{tot}}k \left[\ln \left(\frac{V_{\text{tot}}}{\lambda^3} \right) + \frac{3}{2} \right] - 2Nk \left[\ln \left(\frac{V}{\lambda^3} \right) + \frac{3}{2} \right] \quad (227)$$

$$= 2Nk \left[\ln \left(\frac{2V}{\lambda^3} \right) + \frac{3}{2} \right] - 2Nk \left[\ln \left(\frac{V}{\lambda^3} \right) + \frac{3}{2} \right] \quad (228)$$

$$= 2Nk \ln 2 \quad (\text{wrong}), \quad (229)$$

as compared to $\Delta S = 0$ with the correct expression ([Eq. 223](#)). Does this make sense? Well, imagine going in the reverse direction: simply closing the door. In this case $\Delta S = -2Nk \ln 2$. i.e., we have *decreased* the total entropy, merely by dividing the volume in two. This seems to jar against whatever vague preconceptions we have of the entropy concept.

That treating the particles as distinguishable, by omitting the $1/N!$ factor, results in these entropy changes is known as **Gibb's paradox**.

Gibb's paradox is at odds with a general principle, namely that total entropy should either stay constant or increase with time, which we shall formalize in the next section.

- from our modern perspective, Gibb's paradox isn't really a paradox at all. Electrons do not come stamped with serial numbers, that we could read if we had a good enough "microscope". We have come to accept the fundamental concept of indistinguishable particles, incorporated into quantum mechanics as the symmetrization postulate.

⁶⁰To derive this *incorrect* expression for S , omit the $1/N!$ factor from [Eq. 2.40 of SITP](#) and follow the same steps as Problem 2.31 of SITP.

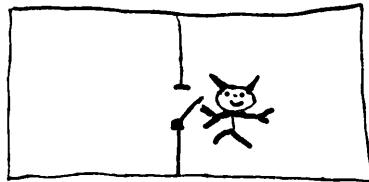
16.3 The 2nd law

- that entropy increases when heat flows from hot to cold, when gases of different types mix, etc..., and that the reverse processes never seem happen spontaneously, leads us to the 2nd law of thermodynamics (in the form due to Planck):

Every process occurring in nature proceeds such that the sum of entropies of all bodies taking part in the process stays the same (a reversible process) or increases (an irreversible process)

$$\Delta S_{\text{universe}} \geq 0 \quad (230)$$

- our microscopic calculations of multiplicity and the fundamental assumption of statistical mechanics lead us to believe that the 2nd law is *statistical*. i.e., a macrostate of higher multiplicity than the current macrostate will be more probable in future.
- attempts to violate the 2nd law always seem to fail, a vivid example being that of **Maxwell's sorting Demon**:⁶¹



Imagine a mixture of He and Ar gas that is spread throughout the two chambers. The “demon” opens the door to let approaching He travel from L to R, and Ar from R to L, “unmixing” the mixture. When analyzed in detail, such a demon always creates more entropy than it destroys.⁶²

16.4 Reversibility, irreversibility, and the chemical potential

- a student is asked to compute the heat released in a chemical reaction, say the production of 1 mol of CO₂ by:



occurring at constant T and P , in such a way that the only work that can be done is expansion/compression work.

The student examines the [physical reference data](#) and finds that values for S have been tabulated for the reactants and products at room T and P . Ignoring the tabulations of standard enthalpies (as discussed in Section 10.2), they compute the heat released from the

⁶¹The original and vastly more popular version of the Demon works on a gas containing a single type of molecule and allows faster going molecules to travel into one chamber and slower going molecules into the other, thereby establishing a temperature differential between the two chambers. The general idea is the same, but I prefer the demon who might help me tidy my office.

⁶²An exhaustive discussion of Maxwell's Demon is given in: H. S. Leff and A. F. Rex, eds., *Maxwell's demon 2 entropy, classical and quantum information, computing* (Institute of Physics Publishing, Bristol, UK, 2003).

reaction by:

$$\begin{aligned} -Q &\stackrel{?}{=} -T\Delta S \\ &\stackrel{?}{=} -T(S(\text{CO}_2) - S(\text{C}) - S(\text{O}_2)), \\ &\stackrel{?}{\approx} -298 \text{ K} \times (213.74 \text{ J/K} - 5.74 \text{ J/K} - 205.14 \text{ J/K}) \times 10^{-3} \text{ kJ/J} \\ &\stackrel{?}{\approx} -0.85 \text{ kJ}. \end{aligned}$$

i.e., $\approx 1 \text{ kJ}$ is *absorbed* from the environment. That does not sound right. In fact the standard enthalpy of formation for one mole of CO_2 is -394 kJ , indicating that 394 kJ will be released. That is a lot different from 1 kJ , which is in fact incorrect, whereas the value given by ΔH is *correct*. Why?

- when we identified $Q = TdS$ for quasi-static processes, we assumed a 1st law of the form

$$dU = TdS - PdV + \text{other forms of work.} \quad (232)$$

In a gas of constant composition, there are generally no other forms of work.⁶³ However, if the amount or composition of the gas can change it turns out that *this possibility may be responsible for work* (a key word being “may”). We account for these additional forms of work with the introduction of a **chemical potential** μ , playing a role similar to pressure, with particle number playing a role similar to volume. For a gas of a single particle type:

$$dU = TdS - PdV + \mu dN \quad (233)$$

so that the definition of the chemical potential is:

$$\mu := \left(\frac{\partial U}{\partial N} \right)_{S,V}. \quad (234)$$

- if a chemical reaction can occur, changing the particle composition in a system, then we must generalize by defining a chemical potential for each particle type, so that if, for example, there were three particle types:

$$dU = TdS - PdV + \mu_1 dN_1 + \mu_2 dN_2 + \mu_3 dN_3 \quad (235)$$

where

$$\mu_1 := \left(\frac{\partial U}{\partial N_1} \right)_{S,V,N_2,N_3} \quad \mu_2 := \left(\frac{\partial U}{\partial N_2} \right)_{S,V,N_1,N_3} \quad \mu_3 := \left(\frac{\partial U}{\partial N_3} \right)_{S,V,N_1,N_2} \quad (236)$$

- if we just mix gases, allow them to react, and then don’t allow other types of work to be done (beyond expansion/compression), then it is no longer true that $Q = TdS$. The unharnessed chemical potential terms also contribute to Q . These terms do contribute to work in electrochemical and fuel cells, as discussed further in Section 24. In the example of the formation of CO_2 that we have given above, the vast discrepancy between the heats suggests that we could — in principle — get most of the heat released out by work instead. More on that later, in Section 24.

⁶³We are excluding the possibility of magnetic and electric work, for which are valid to ignore provided the corresponding fields are not changing.

- (You will find more about the chemical potential and its relation to *diffusive* equilibrium in SITP Section 3.5. Unfortunately although defining the chemical potential, as in Eq. 234, is straightforward, it is rather difficult to show meaningful applications of the concept at this point. My main motivation here — now that you have been introduced to entropy — is to warn you against carefree usage of $Q = TdS$, particularly in the case of chemical reactions.)
- with the introduction of the chemical potential, and the possibility of additional types of work, we now reconsider our example reaction given in Eq. 231, in three scenarios:
 - (1) the reaction is confined to a box of *fixed* volume, but is in thermal equilibrium with its surroundings (infinite heat bath outside box).

The heat absorbed by system is:

$$Q = U_{\text{after}} - U_{\text{before}}. \quad (237)$$

- (2) the reaction can cause the confining box to expand, but does so in equilibrium with constant surrounding pressure P . Likewise, as the reaction occurs, thermal equilibrium is maintained with its surroundings (infinite heat bath outside box).

The heat absorbed by system is:

$$Q = H_{\text{after}} - H_{\text{before}}. \quad (238)$$

- (3) the reaction occurs at a well-defined temperature and pressure, always in both thermal and mechanical equilibrium with its surroundings at T and P , but also *all* additional possible types of work associated with the chemical potential terms are extracted.

The heat absorbed by system is:

$$Q = T(S_{\text{after}} - S_{\text{before}}). \quad (239)$$

In this final case, where the entropy of the system changes by $\Delta S_{\text{system}} = Q/T$, and the surrounding heat reservoir entropy changes by $\Delta S_{\text{reservoir}} = -Q/T$, the net change of the entropy of the universe is

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{reservoir}} \quad (240)$$

$$= 0 \quad (241)$$

This type of process — where the entropy of the universe remains constant, rather than increasing — is known as a **reversible process**. It can never *exactly* occur in practice, but rather is reached in a limiting fashion. The quasi-static isothermal expansion/compression of a gas of constant composition in contact with a thermal reservoir of the same temperature is an example of a reversible process. More examples will be discussed in Part III.

Chemical reactions taking place under quasi-static conditions, in which only expansion/compression work is done (case 2 above) are examples of **irreversible processes**. They are defined as those for which the entropy of the universe, as a whole, increases.

- irreversible doesn't mean "can't be undone". If we have some CO₂ it *is* possible to split it back up into carbon and oxygen. Instead *irreversible* means that we can't undo the process and *return the entire universe back to the same state*; i.e., according to the 2nd law, a change of $\Delta S_{\text{universe}} > 0$ can't be undone. The 2nd law acts like some sort of ratchet as we pass through time.⁶⁴

17 The 3rd law of thermodynamics?

17.1 Introduction

- as evident from their definition, $S := k \ln \Omega$, entropies do not contain arbitrary additive constants in the same way that energy — or at least non-relativistic energy — does. The so-called “3rd law of thermodynamics” is somewhat of a “catch-all” for various aspects of this absolute nature of entropy.
- rather than trying to state the 3rd law — of which there are several variants — we will start by looking at an illustrative example: the meaning of “absolute entropy” in the Sackur-Tetrode equation.

17.2 Sackur-Tetrode revisited

- macroscopic thermodynamics can give us “most” of Sackur-Tetrode without the quantum and mathematical contortions of Section 15.1. Specifically, the ideal gas law and constant C_V for a monatomic ideal gas, are sufficient to compute *differences* in entropy:

$$\Delta S = Nk \ln \left(\left[\frac{T_f}{T_i} \right]^{3/2} \frac{V_f}{V_i} \right) \quad (242)$$

(derivation is a good exercise). Or equivalently:

$$S = Nk \ln(T^{3/2}V) + \text{a constant} \quad (243)$$

where the constant depends on N and the type of atom.

Using $U = \frac{3}{2}NkT$, we may also write:

$$S = Nk \ln(U^{3/2}V) + \text{a constant} \quad (244)$$

which again, is entirely sufficient for computing ΔS .

- if we require that S scale linearly with N , as we keep the temperature and density of the gas constant, then:

$$S = Nk \left[\ln \left(\left[\frac{U}{N} \right]^{3/2} \frac{V}{N} \right) + \text{a constant} \right] \quad (245)$$

where the (different) constant now *only* depends on the type of atom.

⁶⁴We leave further contemplation to philosophers, theologians, and (increasingly) cosmologists.

- comparing to Sackur-Tetrode (Eq. 2.49 of SITP):

$$S = Nk \left[\ln \left(\left[\frac{U}{N} \right]^{3/2} \frac{V}{N} \left[\frac{4\pi m}{3h^2} \right]^{3/2} \right) + \frac{5}{2} \right] \quad (246)$$

we see the additional presence of some “extra parts”:

$$\left[\frac{4\pi m}{3h^2} \right]^{3/2} \quad \text{and} \quad 5/2. \quad (247)$$

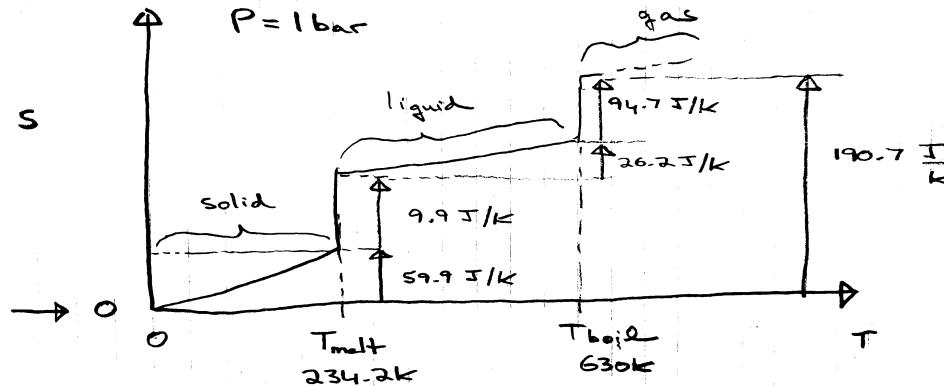
Are these extra parts meaningful?

- let us consider the evaluation of the Sackur-Tetrode equation in the case of mercury (Hg)⁶⁵, with $T = 630 \text{ K}$, $P = 1 \text{ bar}$, and $n = 1 \text{ mol}$:

$$S \approx 190.4 \text{ J/K} \quad (248)$$

(the calculation is the same as SITP Problem 2.33).

- we can also deduce S , under the same conditions, from experimental observations of latent heats for melting and boiling, and the solid and liquid heat capacities, *independently* of Sackur-Tetrode, if we assume that $S = 0$ at $T = 0$:



obtaining $S = 190.7 \text{ J/K}$ which is quite close to the Sackur-Tetrode value 190.4 J/K (close enough to support the legitimacy of the “extra parts” of Eq. 247). For the specifics of this procedure of determining S from heat capacities and latent heats in the case of Ar, see “Sackur and Tetrode are gone” in the [extended example problems](#).

- the preceding comparison between S as given by the Sackur-Tetrode equation, and S as determined by the heat capacities and latent heats depended on setting $S = 0$ at $T = 0$, which is one form of the 3rd law. Setting $S = 0$ at $T = 0$ is reasonable if there is just a *single* “ground-state” of the entire system (corresponding to a multiplicity of $\Omega = 1$, so that $S = 0$). But do all systems always have a single ground state? Or in other words, is the degeneracy of

⁶⁵This example is based on a similar treatment in E. Fermi, *Thermodynamics* (Dover Publications, New York, 1986).

the lowest energy level of a system always 1? That would seem to be a problem of quantum mechanics, for which I have not found an answer in the literature that I am satisfied with.⁶⁶

- to conclude this short, somewhat unsatisfactory treatment, I suggest that we should not view the 3rd law as a component of some sort of thermodynamic trinity, analogous to Newton's laws of mechanics. Instead we should keep in mind the absolute nature of entropy — following from its definition and the underlying quantum mechanical nature of matter. Historically, the 3rd law was developed prior to quantum mechanics, to explain certain macroscopic phenomena,⁶⁷ without the benefit of our current knowledge. This particular piece of physics legislation should be repealed.

18 Microscopic closing words

The purpose of Part II of these notes has been to present the ideas of entropy and temperature with a microscopic justification. This is not the way that the subject developed — the concepts of entropy, temperature and the 2nd law were developed using observations of macroscopic phenomena before the discovery of quantum mechanics.⁶⁸ In contrast, the concepts of quantum mechanics have been used in our treatment (e.g. the quantized levels of the oscillators of the Einstein solid model). Most (but not all) people feel that this is the best approach from a pedagogical point of view.⁶⁹

I must point out that the techniques that we have used for determining the entropy of Einstein solids, ideal gases and two-state paramagnets are *not* the techniques normally used in statistical mechanics (the prediction of macroscopic thermal behaviour from microscopic models). The counting of states (direct determination of the multiplicity) with a fixed system energy is known as the **microcanonical ensemble** approach. In contrast, the **canonical ensemble** (temperature fixed, energy fluctuating) and **grand canonical ensemble** (temperature fixed, energy fluctuating, number of particles fluctuating) are the more powerful and general tools⁷⁰ to predict macroscopic thermal behaviour from microscopic models (e.g. heat capacities, heats of reactions etc...). The development and use of these tools are the subject of Phys 359, Statistical Mechanics.

⁶⁶For further confusion, see: L. Masanes and J. Oppenheim, “A general derivation and quantification of the third law of thermodynamics”, *Nature Communications* **8**, 14538 (2017), which in discomforting frankness states “*We hope the present work puts the 3rd law on a footing more in line with those of the other laws of thermodynamics*”. When it comes to the 3rd law, caveat emptor. I suggest that when someone invokes the 3rd law, you ask them which version that they have in mind.

⁶⁷Some macroscopic observations related to the 3rd law will be discussed in Part III.

⁶⁸For example the heat engines discussed in the next Part of these notes were crucial in the development of the 2nd law in the 1800's — well before quantum mechanics was understood.

⁶⁹Clearly SITP favours this approach, whereas the books by Fermi and Callen mentioned in Section O favour the macroscopic development. Both approaches have their advantages and are worth understanding.

⁷⁰In the canonical and grand canonical ensembles, the problem of determining Ω for fixed energies is avoided. Although determining Ω was relatively straightforward for the Einstein solid and two-state paramagnet, it was not as straightforward for the ideal gas i.e., the justification of $\Omega = N_c(U)$ in Section 15.1. This problem simply does not exist in the canonical and grand-canonical approaches, in which the large- N approximations are “baked-in” to the formalism prior to application to any specific system. Once their general applicability is established, these ensembles are easier to use than the microcanonical ensemble is. If you want to convince yourself that the microcanonical ensemble is difficult to work with, try to analyze a “three-state paramagnet” (each “atom” has three possible energy levels), using the same approach as for the two-state paramagnet. This is not so easy with the microcanonical ensemble — but “trivial” using the canonical ensemble — see Problem 6.22 of SITP.

Nonetheless, the microcanonical ensemble as applied to the specific systems: the Einstein solid, two-state paramagnet and ideal gas, gives a good deal of insight into the formal definitions of entropy and temperature, which you will never need to “unlearn”.

Part III

Macroscopic thermal physics with entropy and the second law

Science has learnt more from the steam engine than the steam engine has learnt from Science

D. G. Wilson et al. in Ref. [1].

19 Introduction

We now return to macroscopic thermodynamics armed with concepts that we were previously missing:

- (1) a new property of systems known as entropy, which yielded
- (2) a definition of temperature, and
- (3) the 2nd law of thermodynamics.

That the 2nd law is an *inequality* will give our arguments a unique flavour not present in other areas of physics.⁷¹ We will be able to rule out certain processes from occurring — as they violate the second law. But in many cases will not be able to say much more. The power of classical macroscopic thermodynamics is its great generality, not the thoroughness of its predictions for any given scenario.

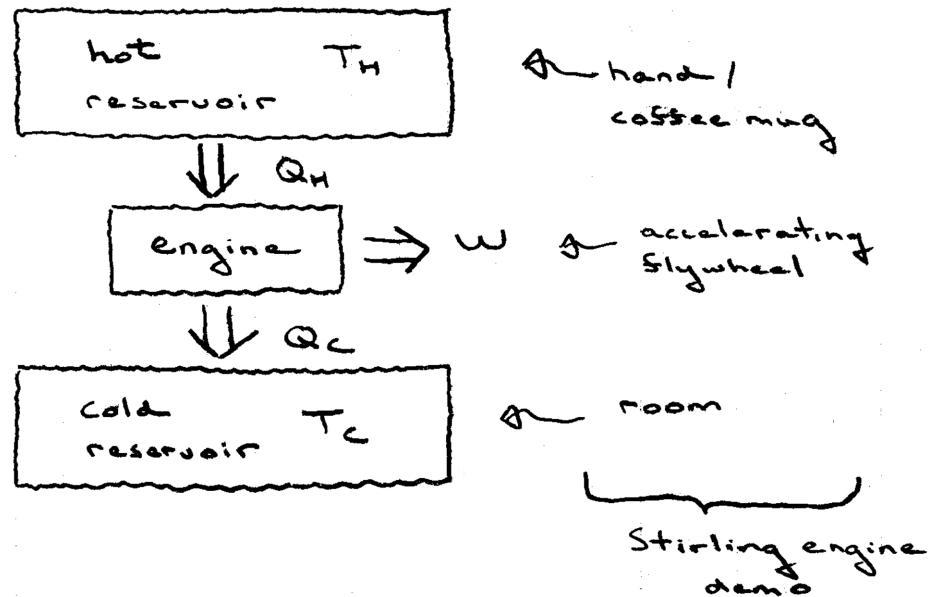
20 Cyclic heat engines (SITP 4.1, 4.3)

20.1 Introduction

- many “engines”
(internal combustion engines in automobiles, steam engines, steam turbines as found in gas and nuclear power plants)

can be understood as doing mechanical work according to the idealization:

⁷¹For example, the famous Heisenberg uncertainty relation is merely a mathematical consequence of $[x, p] = i\hbar$. In contrast, the second law can be viewed as a *fundamental* physical law, expressed as an inequality.



Note that if the engine is the “system”, both W and Q_C are positive for energy flow *out* of system, contrary to the convention that we used when introducing the 1st law (Eq. 37).

Although not explicitly shown in the diagram, the reservoir is constantly being kept hot by some means. For the steam engine in a locomotive: <https://youtu.be/foneS2GhpUg?t=295>. Alternately, the reservoir may have such a large heat capacity so that it effectively stays at the same temperature, despite Q_H flowing out.

- the “Stirling engine” is a wonderful example of a heat engine: <https://youtu.be/Qshc2yWKq2A> (the operation of this device is the subject of Problem 4.21 of SITP), but it is best to defer trying this problem until trying a few simpler heat engine problems). Note that in the video, once the flywheel has been accelerated, the “work” being done is “wasted” as friction. And our hand is being kept at a constant temperature by reactions within our body, compensating for the heat flow out of our hand into the engine (and also room).

The first widespread usage of heat engines was to draw water up and out of flooding mines; but here is a nifty earlier usage:

<https://archive.org/details/RobertStirlingAndTheStirlingMotor?start=246>

If you are from or visiting Hamilton, you may be interested in the [Hamilton Museum of Steam & Technology](#), which is based on the preserved remnants of a large steam engine that used to pump water from Lake Ontario “up the hill” for distribution to the city.

20.2 Constraints on cyclic heat engines due to the 1st and 2nd laws

- we will discuss **cyclic** heat engines: they will return to the same state periodically. In particular, an engine will have no more or less energy at the end of a cycle compared to the start. Consequently, since $\Delta U_{\text{engine}} = 0$, the 1st law tells us that for a complete cycle:

$$Q_H = Q_C + W. \quad (249)$$

- the “engine” will normally be the system for which we will be analyzing the heat flow into and out of, and work that it does. In the following discussion of heat engines we will follow SITP and **temporarily consider W as positive for work being done by the engine and Q_C as positive for heat flowing out of the system** (heat flowing into the engine, Q_H , retains the normal sign convention. The arrows in the diagram above correspond to the directions for energy flows corresponding to positive quantities).⁷²
- maintaining the hot reservoir at T_H (i.e., supplying Q_H) typically “costs” something (e.g., burning fuel), whereas the cold reservoir is typically the surrounding environment.
- with this “cost” perspective, we define **efficiency e** of heat engines as:

$$e := \frac{W}{Q_H} \quad (250)$$

which we can rewrite using the 1st law (Eq. 249) as:

$$e = \frac{Q_H - Q_C}{Q_H} \quad (251)$$

$$= 1 - \frac{Q_C}{Q_H}, \quad (252)$$

a form that will be useful when analyzing specific engine cycles.

- there is a surprising constraint on maximum efficiency based on the 2nd law of thermodynamics:

$$\Delta S_{\text{universe}} \geq 0. \quad (253)$$

- remember that for a quasi-static reversible process: $Q = TdS$. If the reservoir is “large enough” (i.e., has a large heat capacity), then each of the two reservoir temperatures $T_{\text{reservoir}}$ will remain constant as heat is withdrawn and thus:

$$\Delta S_{\text{reservoir}} = \frac{Q}{T_{\text{reservoir}}} \quad (254)$$

so that we can write $\Delta S_{\text{universe}} \geq 0$ as:

$$\underbrace{-\frac{Q_H}{T_H}}_{\substack{\text{entropy decrease} \\ \text{of hot reservoir}}} + \underbrace{\frac{Q_C}{T_C}}_{\substack{\text{entropy increase} \\ \text{of cold reservoir}}} + \Delta S_{\text{engine}} > 0 \quad (255)$$

- we previously argued that for an entire cycle of the engine $\Delta U_{\text{engine}} = 0$. By the same assumption of recurring cyclic operation, it is also the case that $\Delta S_{\text{engine}} = 0$ for a cycle, and thus for an entire cycle:

$$-\frac{Q_H}{T_H} + \frac{Q_C}{T_C} \geq 0. \quad (256)$$

⁷²The wisdom of this switch in convention is not clear to me; however I *do* know that for me not to follow SITP’s choice of conventions (including this temporary switch) would be a *bad idea*.TM

- this inequality explains why a cold reservoir is needed at all. Without the entropy increase of the cold reservoir, the entropy decrease of the hot reservoir would violate $\Delta S_{\text{universe}} \geq 0$. As such, the 2nd law is sometimes stated in the [Kelvin–Planck form](#):

It is impossible to devise a cyclically operating device, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work.

- by examination of Eq. 256 we see that for given Q_H , T_H , and T_C , provided that Q_C exceeds a threshold, it is possible to obey the 2nd law, and do positive work $W = Q_H - Q_C > 0$.
- rearranging Eq. 256, recalling that all quantities are positive — an advantage of switching conventions:

$$\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H} \quad (257)$$

and thus the efficiency (Eq. 250) of any heat engine is bounded; i.e., multiplying both sides by -1 :

$$-\frac{Q_C}{Q_H} \leq -\frac{T_C}{T_H} \quad (258)$$

and adding one to both sides

$$1 - \frac{Q_C}{Q_H} \leq 1 - \frac{T_C}{T_H} \quad (259)$$

so that by the definition of efficiency (Eq. 250)

$e \leq 1 - \frac{T_C}{T_H}.$

(260)

In words: there is an upper bound on the efficiency of heat engines based on the 1st *and* 2nd law of thermodynamics.

- as an example of some numbers: the manufacturer's instructions for the Stirling engine that I normally demonstrate in the lectures (similar to the linked video) says that a temperature difference of $\Delta T \approx 4\text{ K}$ is necessary for operation. That is readily achieved through the temperature difference between a human hand and the surrounding room. Let's say:

$$T_C = 300\text{ K}, \text{ and} \quad (261)$$

$$T_H = 304\text{ K} \quad (262)$$

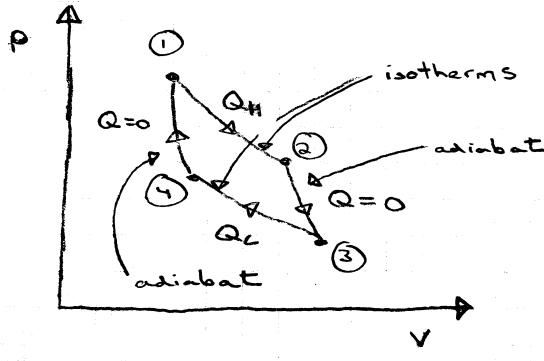
so that by Eq. 260

$$e \leq 1 - \frac{300}{304} \quad (263)$$

$$\leq 0.013 \quad (264)$$

i.e., only a maximum of $\approx 1\%$ of energy extracted from the hot reservoir *may* end up as work.

- for most practical engine cycles we will find that we may improve their efficiency by increasing T_H , as we might expect from Eq. 260.⁷³ In fact, thermodynamics developed alongside and in aid of improving the efficiency of steam engines.
- 
- the so-called **Carnot cycle** approaches the maximum achievable thermodynamic efficiency for heat engine operating between reservoirs at T_H and T_C . Here is the indicator diagram for the working material of the engine:



In deriving the general constraint on efficiency given by Eq. 260 we considered the changes in entropy of the reservoirs and for the engine only needed to consider that for a complete cycle $\Delta S_{\text{engine}} = 0$. To analyze the Carnot cycle we explicitly consider the changes in the entropy of the engine that give $\Delta S_{\text{engine}} = 0$ for the whole cycle.

The two adiabats result in no entropy change of the engine — or more precisely the working material of the engine.

What about the two isotherms? When drawing heat in at T_H , the entropy of the engine changes by $\Delta S_{\text{engine}} = Q_H/T_H$. When expelling heat at T_C , the entropy of the engine decreases by $\Delta S_{\text{engine}} = -Q_C/T_C$. Thus the total change in entropy of the engine is $\Delta S_{\text{engine}} = Q_H/T_H - Q_C/T_C$. Since the engine is cyclic, $\Delta S_{\text{engine}} = 0$, and thus

$$\frac{Q_C}{T_C} = \frac{Q_H}{T_H}, \quad (265)$$

so equivalently

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H}, \quad (266)$$

and thus by Eq. 252:

$e_{\text{Carnot}} = 1 - \frac{T_C}{T_H}$

(267)

Notice that we have not assumed anything about the working material of the engine. For an explicit confirmation of Eq. 267 when the working fluid is an ideal gas, see the SITP Problem 4.5.

⁷³You might hear people say that the Stirling engine is efficient because it works on such a small temperature difference. That is open to misinterpretation. It is more precise to say: since the Stirling engine is so efficient (i.e., close to the thermodynamic limit) it can work using small temperature differences.

- the problem with the achieving Carnot cycle efficiencies is that temperature *differences* are needed for heat to flow. More specifically, for heat to flow into the working fluid, its temperature T_H should be slightly *less* than the hot reservoir temperature, and for heat to flow out of the working material, its temperature should be *greater* than the cold reservoir temperature. If we are given two reservoirs to work with, one at T_C , the other at T_H (with $T_C < T_H$), then for heat to flow spontaneously in and out of the engine from and to the reservoirs, we need the temperatures of our working material during the two isothermal steps, T_{HW} and T_{CW} (with $T_{CW} < T_{HW}$) to satisfy:

$$T_C < T_{CW} < T_{HW} < T_H \quad (268)$$

Then the actual efficiency of the engine will always be less than the theoretical maximum efficiency achievable with the two reservoirs:

$$1 - \frac{T_{CW}}{T_{HW}} < 1 - \frac{T_C}{T_H} \quad (269)$$

as a consequence of Eq. 268.

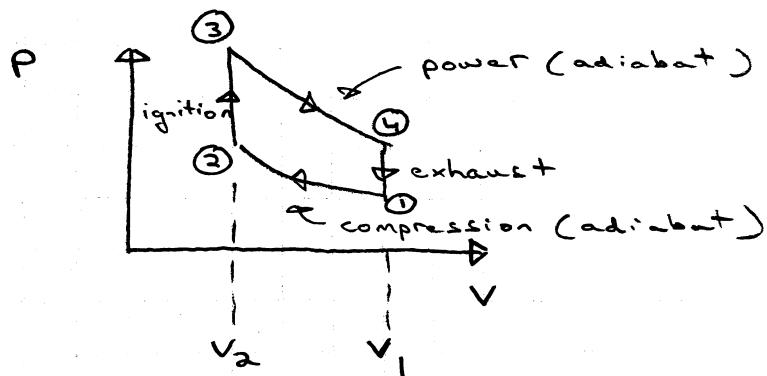
The closer that we can get the working fluid temperatures closer to the reservoir temperatures, the closer to the ideal Carnot efficiency we will get, but the slower the engine will operate (due to reduced rates of heat flow).

An interesting way to analyze this trade-off between power output and efficiency is given by [Problem 4.6 of SITP](#). (A subject sometimes known as **finite-time thermodynamics**.)

- in practice, although the Carnot cycle approaches the maximum possible efficiency consistent with the 2nd law, it is generally *not* the basis of operation for most heat engines. We shall now study some more practical cycles.

20.3 Internal combustion engines (SITP 4.3)

-
- gasoline engines, such as those in most automobiles, may be approximately understood as heat engines, operating according to the **Otto cycle**:



- there are several inaccurate aspects of this idealization — but nonetheless it does provide insight, particularly with regards to the relative efficiencies of Diesel and gasoline engines.⁷⁴
- what is the thermodynamic efficiency e_{otto} of such engines? i.e., some fuel is being burned to heat the air up in steps $2 \rightarrow 3$. How much work do we get out (the total enclosed area for a cycle), and how does this compare to the Carnot efficiency ($e_{\text{carnot}} = 1 - T_C/T_H$)?
- we rewrite $e_{\text{Otto}} := W/Q_H$ using the 1st law as

$$e_{\text{Otto}} = 1 - \frac{Q_C}{Q_H} \quad (270)$$

and these heats are absorbed/released during isochoric processes, so that:

$$Q_C = C_V(T_4 - T_1) \quad (271)$$

and

$$Q_H = C_V(T_3 - T_2). \quad (272)$$

Substituting into Eq. 270, gives:

$$e_{\text{Otto}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} \quad (273)$$

The temperature difference ratio may be written in terms of V_2 and V_1 (which are determined by the geometry of the cylinders and pistons of the engine). More specifically, from the two adiabats we have (from Eq. 83):

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} \text{ compression} \quad (274)$$

and

$$\frac{T_3}{T_4} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} \text{ expansion} \quad (275)$$

Let's use these to rewrite $T_3 - T_2$ in terms of T_4 and T_1 :

$$T_3 - T_2 = \left(\frac{V_1}{V_2} \right)^{\gamma-1} T_4 - \left(\frac{V_1}{V_2} \right)^{\gamma-1} T_1 \quad (276)$$

$$= \left(\frac{V_1}{V_2} \right)^{\gamma-1} (T_4 - T_1) \quad (277)$$

and thus Eq. 273 becomes:

$$e_{\text{Otto}} = 1 - \frac{T_4 - T_1}{\left(\frac{V_1}{V_2} \right)^{\gamma-1} (T_4 - T_1)} \quad (278)$$

$$e_{\text{Otto}} = 1 - \left(\frac{V_2}{V_1} \right)^{\gamma-1},$$

(279)

⁷⁴Obviously there are lots of books on internal combustion engines written for engineers. One with a more “scientific” bent than normal is R. Stone, *Introduction to internal combustion engines*, 4. ed (Palgrave Macmillan, Basingstoke, 2012).

an impressively tidy result.

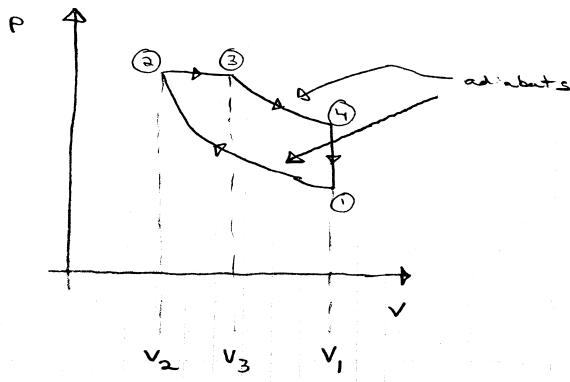
- the quantity V_1/V_2 is known as the **compression ratio**. It is typically ≈ 8 for automobile engines. With $\gamma = 7/5$ for air near room-temperature (Section 8.3):

$$e_{\text{Otto}} \approx 1 - \left(\frac{1}{8}\right)^{7/5-1} \quad (280)$$

$$\approx 0.56. \quad (281)$$

The actual efficiency will be lower due to friction and the various idealizations of the Otto cycle.

- Equation 279 shows us that increasing the compression ratio will improve efficiency, raising the temperature at the end of the compression stroke. But the problem is **preignition** in the compression phase; i.e., the air-fuel mixture may *spontaneously* ignite during the compression phase, retarding the piston, before the spark plug fires near “top dead centre”.
-
-
- Diesel engines**⁷⁵ avoid pre-ignition by compressing air alone, and then injecting fuel into the hot air at high compression, negating the need for a spark plug.
- the Diesel cycle is similar to the Otto cycle, but with the idealization that combustion now occurs at constant *pressure* ($2 \rightarrow 3$), not volume:



- again we can determine a thermodynamic efficiency for the Diesel cycle. As before, we characterize the cycle by the compression ratio V_1/V_2 , but now also introduce the **cut-off ratio** := V_3/V_2 . As we shall now show, the efficiency

$$e_{\text{Diesel}} = W/Q_H \quad (282)$$

$$= 1 - \frac{Q_C}{Q_H} \quad (283)$$

⁷⁵There was a Mr. Diesel and his story shows that inspiration may come from unexpected places. Like many inventors before and after him, his passage through life was not a calm one <https://www.bbc.com/news/business-38302874>.

can be written in terms of these two quantities.

Again, like for the Otto cycle:

$$Q_C = C_V(T_4 - T_1). \quad (284)$$

But for Q_H we must use C_P , as $2 \rightarrow 3$ is isobaric:

$$Q_H = C_P(T_3 - T_2) \quad (285)$$

Again, like in the Otto cycle case, the adiabats $1 \rightarrow 2$ and $3 \rightarrow 4$ give us

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} \text{ compression} \quad (286)$$

and

$$\frac{T_3}{T_4} = \left(\frac{V_4}{V_3} \right)^{\gamma-1} \text{ expansion.} \quad (287)$$

And since $V_4 = V_1$, we may rewrite this as:

$$\frac{T_3}{T_4} = \left(\frac{V_1}{V_3} \right)^{\gamma-1}. \quad (288)$$

Using these results in Eq. 283 gives:

$$e_{\text{diesel}} = 1 = \frac{C_V(T_4 - T_1)}{C_P(T_3 - T_2)} \quad (289)$$

$$= 1 - \frac{1}{\gamma} \left[\frac{T_3 \left(\frac{V_3}{V_1} \right)^{\gamma-1} - T_2 \left(\frac{V_2}{V_1} \right)^{\gamma-1}}{T_3 - T_2} \right] \quad (290)$$

and factor out T_2 from numerator and denominator in the second term to give:

$$e_{\text{diesel}} = 1 - \frac{1}{\gamma} \left[\frac{\frac{T_3}{T_2} \left(\frac{V_3}{V_1} \right)^{\gamma-1} - \left(\frac{V_2}{V_1} \right)^{\gamma-1}}{\frac{T_3}{T_2} - 1} \right] \quad (291)$$

We may determine T_3/T_2 from the fact that $2 \rightarrow 3$ is isobaric, and thus

$$\frac{T_3}{T_2} = \frac{V_3}{V_2} \quad (292)$$

giving

$$e_{\text{Diesel}} = 1 - \frac{1}{\gamma} \left[\frac{\frac{V_3}{V_2} \left(\frac{V_3}{V_1} \right)^{\gamma-1} - \left(\frac{V_2}{V_1} \right)^{\gamma-1}}{\frac{V_3}{V_2} - 1} \right]. \quad (293)$$

We may write

$$\frac{V_3}{V_1} = \frac{V_3}{V_2} \frac{V_2}{V_1} \quad (294)$$

so that finally

$$e_{\text{Diesel}} = 1 - \frac{1}{\gamma} \left[\frac{\frac{V_3}{V_2} \left(\frac{V_3}{V_2} \frac{V_2}{V_1} \right)^{\gamma-1} - \left(\frac{V_2}{V_1} \right)^{\gamma-1}}{\frac{V_3}{V_2} - 1} \right] \quad (295)$$

$$e_{\text{Diesel}} = 1 - \frac{1}{\gamma} \left(\frac{V_2}{V_1} \right)^{\gamma-1} \left(\frac{\left(\frac{V_3}{V_2} \right)^\gamma - 1}{\frac{V_3}{V_2} - 1} \right), \quad (296)$$

a somewhat messy result.⁷⁶

- comparing e_{Diesel} to e_{Otto} , it is possible to show that *for the same compression ratio* (V_1/V_2), we have $e_{\text{Diesel}} < e_{\text{Otto}}$ (a good, not completely straightforward exercise). However, since the Diesel can use higher compression ratios (avoiding preignition), in practice: $e_{\text{Diesel}} > e_{\text{Otto}}$. e.g., some typical numbers:

V_1/V_2	e_{Otto}	e_{Diesel} (with $V_3/V_2 = 2$)
8	0.56	0.49
18	0.69	0.63

where the high compression ratio for the Otto cycle is considered infeasible (0.69). Given this restriction, the thermodynamic efficiency of diesel engines is typically higher than that of spark ignition engines; i.e., the Otto cycle. But thermodynamic efficiency is not the only metric of engine performance.⁷⁷

20.4 Steam turbines (SITP 4.3)

- internal combustion engines will eventually go the way of the dodo bird.⁷⁸ However, heat engines — in the form of steam turbines — are probably here to stay, as they are currently used in fission plants, and may be used (although not necessarily) in fusion power.
- from the physics point of view, the interesting aspect of the study of steam turbines is their usage of a *non-ideal* fluid (water vapour and liquid) that undergoes changes of phase in the engine cycle. Unlike ideal gas working fluids, the material properties are not easily handled by a few simple formulae. These properties used to be tabulated — engineer’s beloved “steam tables”. Of course, now that is all best handled with computers (see Appendix G).
- the key points of interest also appear in studies of either refrigeration, and/or the liquification of gases; so I’ve provided a brief treatment later on (in Section 22.3).

⁷⁶In agreement with Heywood, *Internal combustion engine fundamentals* if we set $r_c = V_1/V_2$, $\beta = V_3/V_2$ and $\alpha = 1$ in his Eq. 5.43 (pg 172).

⁷⁷Why do most trucks use Diesel engines, but most cars do not? The video [Why Diesel cars are disappearing](#) is quite informative.

⁷⁸Well, either them or us.

21 Interlude — Are we heat engines?

<https://xkcd.com/793/>

- the thermodynamic constraints on heat engines are so elegant, that it is tempting — like the proverbial man with hammer — to find heat engines everywhere. Answering the question posed in this section’s title⁷⁹ will temper that sort of excessive enthusiasm.
- we consume oxygen and expel carbon dioxide, suggesting that we obtain our energy from a process similar to the combustion of hydrocarbons, such as that of gasoline in an automobile. Measuring the heat released by burning food (how calorie content is determined — see https://en.wikipedia.org/wiki/Food_energy#Measure) and comparing this to the mechanical work that we can do for the same amount of food gives:

$$\frac{W}{Q_{\text{combustion}}} \approx 0.25. \quad (297)$$

Suppose that our internal operation was that of a heat engine. In this case we know that the efficiency e must satisfy:

$$e \leq 1 - \frac{T_C}{T_H}. \quad (298)$$

We expel heat into an environment at roughly $T_C \approx 300\text{ K}$. Combining this constraint with Eq. 297 gives us a *lower* bound on T_H :

$$0.25 \leq 1 - \frac{300\text{ K}}{T_H} \quad (299)$$

$$\frac{300\text{ K}}{T_H} \leq 0.75 \quad (300)$$

$$400\text{ K} \leq T_H. \quad (301)$$

But this implies that we have internal body temperatures greater than the boiling point of water. That doesn’t seem likely.

- have our bodies found a way to violate the 2nd law of thermodynamics? Betteridge says no. We are not “heat engines”, but more like “fuel cells/batteries”, which we shall discuss later in Section 24.2.
- for now, I point out that whenever we have used:

$$Q = \Delta H \quad (302)$$

for a process, we are assuming that the *only* work being done was due changing volume in a constant pressure environment. i.e., under this condition:

$$\Delta U = Q + W \quad (303)$$

$$= Q - P\Delta V \quad (304)$$

⁷⁹ This section’s title, content, and numbers are based on D. G. Wilson et al., *Bicycling science*, Fourth edition (The MIT Press, Cambridge, Massachusetts ; London, England, 2020).

so that

$$Q = \Delta U + P\Delta V \quad (305)$$

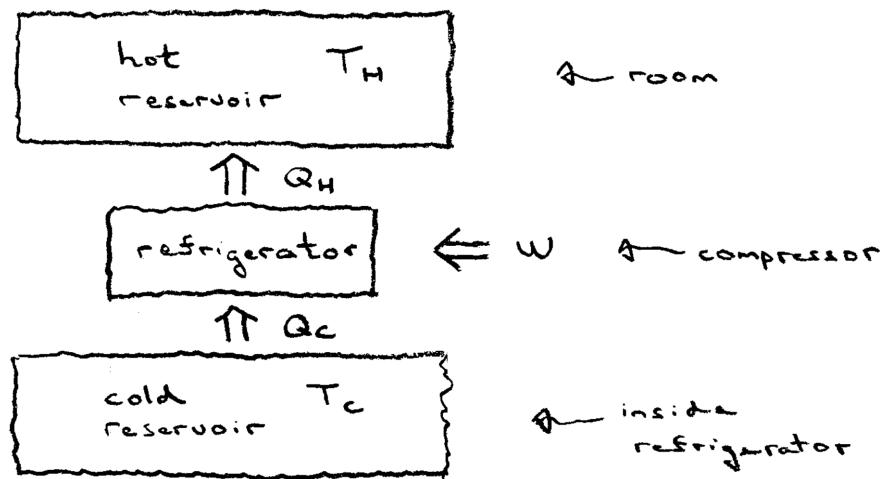
$$= \Delta H. \quad (306)$$

But other types of work can be done by a chemical reaction (i.e., electrical work by a battery) so that $W \neq -P\Delta V$, and thus $Q \neq \Delta H$ in general.

22 Cyclic refrigerators (SITP 4.2, 4.4)

22.1 Introduction

- the constraints on the operation of refrigerators due to the laws of thermodynamics are similar to those for heat engines. In a sense, a refrigerator is a heat engine operating “in reverse” (cf. [heat engine equivalent](#)):



Although we don't show it in the diagram, heat is constantly flowing into the cold reservoir from the room, due to imperfect thermal insulation. To keep the cold reservoir at the same temperature, the refrigerator should continuously draw heat out of the cold reservoir (Q_C shown above). (In analogy, recall that in the heat engine, normally fuel is burned to keep the hot reservoir at a constant temperature.)

- the directions of the arrows indicate the conventions for positive values of the quantities: Q_C , Q_H and W . Note that Q_C and W have the same convention as normal (flowing into the refrigerator), whereas for the following discussion of refrigerators — for consistency with SITP — **we temporarily adopt the convention that Q_H corresponds to positive heat flow out of the system (refrigerator)**.
- we are no longer interested in e as was defined for heat engines. Instead, we want to expend minimal W for maximal Q_C , and thus want a high **coefficient of performance**:

$$COP := \frac{Q_C}{W} \quad (307)$$

- what constraints do the 1st and 2nd laws place on the *COP*?
- again, as with heat engines, we assume cyclic operation, so that by the 1st law, $W = Q_H - Q_C$, and thus

$$COP = \frac{Q_C}{Q_H - Q_C} \quad (308)$$

$$= \frac{1}{Q_H/Q_C - 1} \quad (309)$$

but $\Delta S_{\text{universe}} \geq 0$ implies

$$\frac{Q_H}{Q_C} - \frac{T_H}{T_C} \geq 0. \quad (310)$$

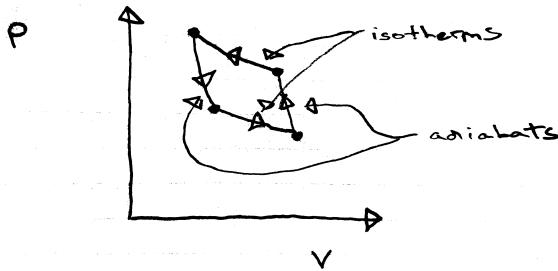
So

$$\frac{Q_H}{Q_C} \geq \frac{T_H}{T_C} \quad (311)$$

and thus combining with Eq. 309 we have the constraint:

$$COP \leq \frac{1}{T_H/T_C - 1} \quad (312)$$

- note that for high *COP*, the reservoir temperatures T_C and T_H should be as close as possible (in contrast with heat engines, where the reservoir temperatures should be “far apart” for high e). And it is possible that $COP > 1$, whereas for a heat engine it is always true that $e \leq 1$.
- in fact the inequality of Eq. 312 is **saturated** (attains equality) by running the Carnot cycle in “reverse”:



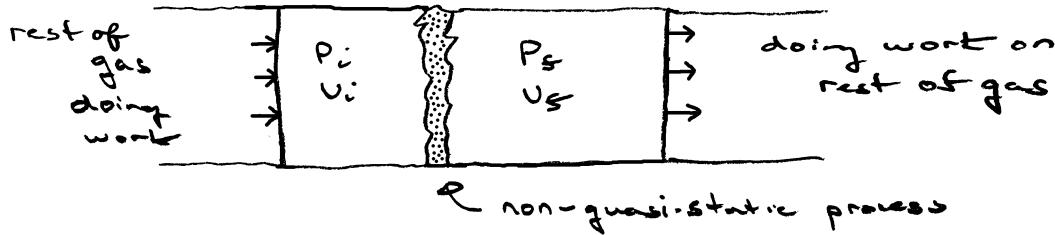
Again, as for heat engines, in practice the Carnot efficiency may only be achieved in a limiting sense, at the expense of low refrigerating power.

- so for practical reasons, as in the case of heat engines, the Carnot cycle is rarely used. Analysis of the most common cycle is somewhat similar to that of the steam turbine “in reverse”. However, there is now a device known as a **throttle**, which must be understood.

Examples: SITP Problem 4.17, Impossible refrigerator, and SITP Problem 4.15, Absorption refrigerator.

22.2 Throttling in refrigeration

- the gas goes in one side of throttle at pressure P_i and emerges at the other side at pressure P_f , also changing its volume from V_i to V_f :



- starting from the 1st law:

$$\Delta U = Q + W, \quad (313)$$

we assume that $Q = 0$ during the throttling process.

- work is done by the gas on both sides of the throttle:

$$W = P_i V_i - P_f V_f \quad (314)$$

and thus

$$\Delta U = P_i V_i - P_f V_f \quad (315)$$

$$U_f - U_i = P_i V_i - P_f V_f \quad (316)$$

Rearranging gives:

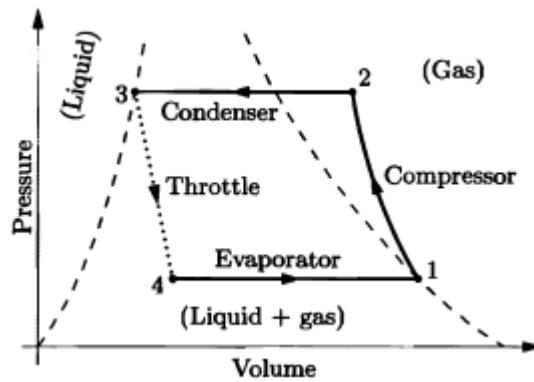
$$U_f + P_f V_f = U_i + P_i V_i. \quad (317)$$

Since enthalpy is defined as $H := U + PV$ (Eq. 88), we see that enthalpy is conserved in the throttling process i.e., $\Delta H = 0$. This constant enthalpy throttling is also commonly referred to as a **Joule-Thomson** process.

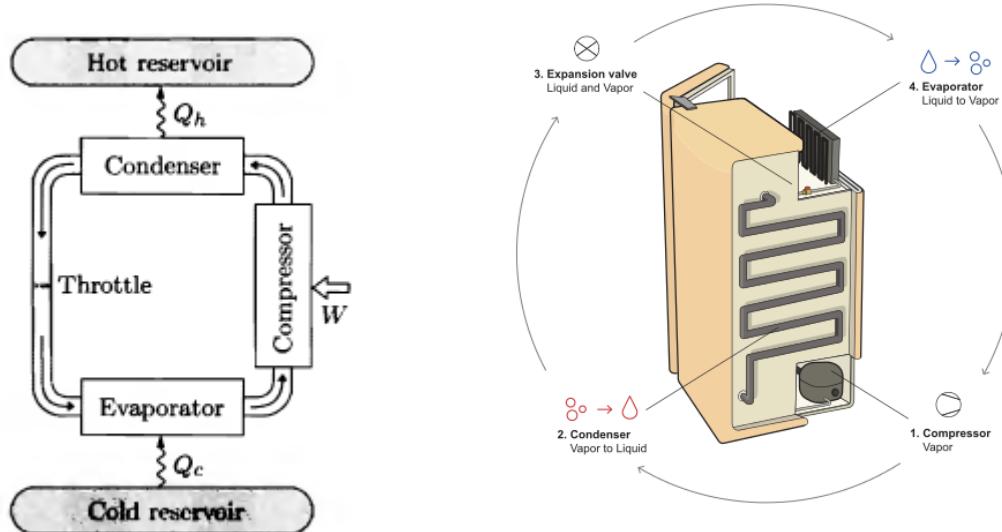
- note that for an ideal gas, $\Delta H = 0$ implies $\Delta T = 0$, so that throttling does not lead to a temperature reduction. (You should be able to argue that this is true.)
- now let us consider how throttling differs from our idealized view of passage through a steam turbine. In that case, $Q = 0$ as well, but we assumed that the gas passed through a series of equilibrium states, doing work as it expanded, so that $\Delta S = 0$. By contrast, the throttling process is not quasi-static, and we represent this process by a “dotted line” on indicator diagrams.

22.3 Analysis of a real refrigeration cycle using throttling

- consider a fluid undergoing the cycle (Fig. 4.9 of SITP):



by passing through the system (Fig. 4.9 of SITP and [Daniele De Pietri, DensityDesign Research Lab](#)):



In between the dotted lines, the working fluid is a *mixture* of gas and liquid. As we go around the cycle, the working material changes phase:

- in 1 it is a saturated gas
- in 2 it is a superheated gas
- in 3 it is a saturated liquid
- in 4 it is a liquid and gas mixture

where the term **saturated** means that the fluid is on the verge of boiling or condensing, and the term **superheated** refers to a gas not at condensation e.g., water at 120 °C and 1 bar (see this [demo](#)).

- we will determine the COP (Eq. 307) for a refrigerator for this type of cycle using (Eq. 309):

$$COP = \frac{Q_C}{Q_H - Q_C}. \quad (318)$$

Remember that changes in enthalpy tell us heat flow for constant pressure processes, so that:

$$Q_C = H_1 - H_4 \quad (319)$$

and

$$Q_H = H_2 - H_3. \quad (320)$$

Substituting into Eq. 318 gives:

$$COP = \frac{H_1 - H_4}{H_2 - H_3 - (H_1 - H_4)}. \quad (321)$$

And since throttling is a constant enthalpy process, $H_3 = H_4$, so that:

$$COP = \frac{H_1 - H_3}{H_2 - H_1}. \quad (322)$$

To proceed we need to know the enthalpies and entropies of the working fluid — the so-called **refrigerant**. For the common (at least when SITP was written) refrigerant HFC-134a, see Tables 4.3 and 4.4 of SITP (reproduced in the [Reference data](#) section). Nowadays the required refrigerant properties — as with those for water required for steam turbine analysis — would be accessed using computer programs (see Appendix G).

Label the two extreme pressures P_{low} ($= P_1 = P_4$) and P_{high} ($= P_2 = P_3$).

To determine the COP:

1. look up H_1 and S_1 in Table 4.3 of SITP. i.e., H_{gas} and S_{gas} at P_{low} .
2. assume that $S_1 = S_2$, since the step $1 \rightarrow 2$ is quasi-static and adiabatic. Determine the temperature that gives an (unsaturated) gas of the refrigerant with entropy S_2 at P_{high} , from Table 4.4 of SITP. Note the value of H_2 under these conditions (also from Table 4.4 of SITP).
3. look up H_3 from Table 4.3 of SITP i.e., H_{liquid} at P_{high} .
4. substitute the determined values of H_1 , H_2 and H_3 into the expression for the COP (Eq. 322).

Example: SITP Problem 4.31, Household air conditioner

23 Entropy and the 2nd law for non-cyclic systems

23.1 Helmholtz free energy

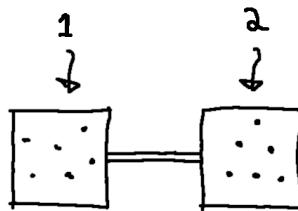
- our idealizations of heat engines and refrigerators involved cyclic systems: the system state continually cycles, changing its energy and entropy but periodically *returning* to the same state, with the same energy and entropy and so-on. We analyzed efficiencies and coefficients

of performance by considering an entire cycle, as that is what will ultimately be relevant after averaging over many cycles.

As both the heat engines and refrigerators operated, their internal entropy continuously cycled showing no net increase or decrease over time. But the entropy of the heat reservoirs, and thus universe, generally increased over time as required by the second law; the option of the entropy staying the same being generally impractical for actual devices.

In this section, we apply the second law to *non-cyclic* situations, and will pay close attention to the initial and final states of the entropy of the *system* and its contribution to the entropy of the universe.

- let us imagine two containers filled with a gas and connected by a small tube:



- this entire system is in thermal contact with a reservoir at a constant temperature. The “universe” is the surrounding reservoir and the system.
- common sense tells us that the pressure inside each of the volumes should be the same, otherwise there would be some flow of gas from one container to another. However, it is useful to arrive at the same conclusion in a different way, applicable when the connecting tube is so small that the concept of pressure in the tube is dubious due to the small average number of molecules contained within.
- let us assume the gas to be a monatomic ideal gas so that its entropy is described by the Sackur-Tetrode equation:

$$S(N, V, T) = Nk \left[\ln \left(\frac{V}{N} \frac{1}{\lambda^3} \right) + \frac{5}{2} \right] \quad \text{with} \quad \lambda := \sqrt{\frac{2\pi\hbar^2}{mkT}}, \quad (323)$$

where m is the mass of the each of the atoms.

- the total entropy of the system is given by:

$$S_{\text{system}} = S(N_1, V_1, T) + S(N_2, V_2, T) \quad (324)$$

But since the total number of atoms N is fixed, so that $N_1 = N - N_2$, we will write this as:

$$S_{\text{system}} = S(N - N_2, V_1, T) + S(N_2, V_2, T) \quad (325)$$

We now consider maximizing this entropy by varying the number of particles in each volume, as characterized by N_2 . It is important to note that as N_2 varied, no energy is lost or gained

by the system to the outside world, as the internal energy of an ideal gas is dictated solely by its temperature (recall Joule's experiment, Fig. 7). Thus as N_2 varies, no energy enters or exits the system from the surrounding reservoir, so we do not need to consider the change in entropy of the surrounding reservoir. As a consequence, maximizing the entropy of the system is the equivalent to maximizing the entropy of the universe.

- to differentiate Eq. 325, we first note that differentiating Eq. 323 wrt N gives:

$$\frac{1}{k} \frac{dS}{dN} = \ln\left(\frac{V}{N\lambda^3}\right) + \frac{3}{2} \quad (326)$$

so that starting with Eq. 325 we obtain:

$$\frac{dS_{\text{system}}}{dN_2} = \frac{dS_1}{dN_2} + \frac{dS_2}{dN_2} \quad (327)$$

$$= \frac{dN_1}{dN_2} \frac{dS_1}{dN_1} + \frac{dS_2}{dN_2} \quad (328)$$

$$= -\frac{dS_1}{dN_1} + \frac{dS_2}{dN_2} \quad (329)$$

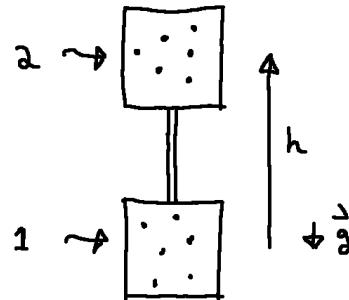
$$= k \left[-\ln\left(\frac{V_1}{N_1\lambda^3}\right) - \frac{3}{2} + \ln\left(\frac{V_2}{N_2\lambda^3}\right) + \frac{3}{2} \right]. \quad (330)$$

Setting equal to zero for an extremum and rearrange to obtain:

$$\frac{V_1}{N_1} = \frac{V_2}{N_2} \quad (331)$$

which since $T_1 = T_2 = T$ implies $P_1 = P_2$, by the ideal gas law.

- now let us slightly complicate this two volume system: consider the two volumes to be displaced from one another vertically by distance h in a gravitational field, so that mgh worth of energy is required to move a particle from volume 1 to volume 2:



For concreteness, we will choose the “zero” of energy to correspond to the lower volume, so that the total system energy is:

$$U_{\text{system}} = N_2 mgh + \frac{3}{2} N k T. \quad (332)$$

Now — unlike the first example of volumes at the same height — there *is* an energy cost associated with moving atoms from one volume to another. Since the kinetic energy of the atoms remains the same (remember that the atoms are in thermal contact with the reservoir):

1. one atom moving from V_2 to V_1 will give mgh worth of energy to the reservoir.
2. one atom moving from V_1 to V_2 will take mgh worth of energy from the reservoir.

Since the volume of the gas system is fixed, there is no way to exchange energy with the reservoir as work. It has to be heat, so that $\Delta U = Q$, and thus each gain or loss of energy by the reservoir is accompanied by an entropy change of the reservoir $\Delta S_{\text{reservoir}} = \Delta U_{\text{reservoir}}/T$. If that was the only relevant entropy (it is not), the second law would favour *all* of the atoms being in the lower reservoir as that correspond the largest possible entropy of the external reservoir.

- however, as we have seen from the case of *no* gravitational field, the maximizing the entropy of the *gas* requires the number of atoms in each volume to be proportional to the volume.
- thus there is a competition between two ways to increase the entropy of the *universe*, which includes *both* the reservoir and the system. The equilibrium values of N_1 and N_2 must be decided on the basis of this competition. i.e., the maximization of the universe's entropy:

$$S_{\text{universe}} = S_{\text{system}} + S_{\text{reservoir}} \quad (333)$$

Again, as in the case of volumes at the same heights, the entire state is represented by N_2 , and thus we differentiate wrt to N_2 with the anticipation of setting this derivative equal to zero:

$$\frac{dS_{\text{universe}}}{dN_2} = \frac{dS_{\text{system}}}{dN_2} + \frac{dS_{\text{reservoir}}}{dN_2} \quad (334)$$

$$= \frac{dS_{\text{system}}}{dN_2} + \frac{1}{T} \frac{dU_{\text{reservoir}}}{dN_2} \quad (335)$$

$$= \frac{dS_{\text{system}}}{dN_2} - \frac{1}{T} \frac{dU_{\text{system}}}{dN_2} \quad (336)$$

$$= -\frac{1}{T} \left(-T \frac{dS_{\text{system}}}{dN_2} + \frac{dU_{\text{system}}}{dN_2} \right) \quad (337)$$

$$= -\frac{1}{T} \frac{d}{dN_2} (U_{\text{system}} - TS_{\text{system}}). \quad (338)$$

It is customary to introduce the **Helmholtz free energy** $F_{\text{system}} := U_{\text{system}} - TS_{\text{system}}$, so that:

$$\frac{dS_{\text{universe}}}{dN_2} = -\frac{1}{T} \frac{dF_{\text{system}}}{dN_2}. \quad (339)$$

Our manipulations show that the maximization of the universe's entropy (system and reservoir) is equivalent to the minimization of the Helmholtz free energy of the *system*.

- one might ask: why we did not just stop at Eq. 336? i.e., why factor out the $-1/T$ and introduce the Helmholtz free energy instead of referring to the universe's total entropy? We

will see later, in Section 24, that changes in F_{system} for a process acquire a special significance, giving us an indication of the maximum amount of non-mechanical work that can be done in processes.⁸⁰ There is also a slight similarity in the form $F := U - TS$ to that of the enthalpy $H := U + PV$. Later, in Section 25.1, we shall see that this similarity in form gives a sort of “unified theory” and set of techniques for handling H , F , and similar quantities.

For now, the important point is that for a constant volume system in thermal equilibrium with a reservoir at temperature T , minimizing F_{system} is equivalent to maximizing the total entropy of the universe.

- now let us return to the specifics of this two volume system by substituting the relevant expressions for U_{system} and S_{system} :

$$\frac{dF_{\text{system}}}{dN_2} = \frac{dU_{\text{system}}}{dN_2} - T \frac{dS_{\text{system}}}{dN_2} \quad (340)$$

$$= mgh - kT \left[-\ln \left(\frac{V_1}{N_1 \lambda^3} \right) + \ln \left(\frac{V_2}{N_2 \lambda^3} \right) \right] \quad (341)$$

$$= mgh - kT \ln \left(\frac{N_1/V_1}{N_2/V_2} \right). \quad (342)$$

Setting this derivative equal to zero and rearranging gives:

$$\boxed{\frac{N_2/V_2}{N_1/V_1} = e^{-mgh/(kT)}} \quad (343)$$

- the ideal gas law allows us to write $N/V = P/(kT)$, so that

$$\frac{P_2}{P_1} = e^{-mgh/(kT)} \quad (344)$$

which is the familiar variation of atmospheric pressure with altitude. However, our rationalization is quite different here — as pointed out before, the tube can be so small that pressure inside the tube is ill-defined. Our argument here was based on the second law of thermodynamics, and illustrates the trade-off in maximizing entropy, and the motivation for the definition of free energy of a system.

- the minimization of the universe’s entropy by maximizing a system’s Helmholtz free energy is rather fundamental. Many problems can be tackled using this principle; e.g., surface coverage in the presence of a gas and the extent of ionization in stellar atmospheres.⁸¹ Of course the variable “ N_2 ” — describing the distribution of the gas within the two volumes — will be replaced by other “internal variables” describing the state of the system. These internal variables should be varied to minimize the Helmholtz free energy.

⁸⁰In SITP, Schroeder chooses the opposite order of presentation, emphasizing the work aspect first.

⁸¹These applications were the problems: “Pockets for atoms” on Test 6 for Phys 358, Fall 2020, and “An unpleasant subject” on Test 6 for Phys 358, Spring 2020.

- a remark on notation: in this section I have been explicit about labelling the system, reservoir, and universe quantities. However, the Helmholtz free energy is normally written as $F = U - TS$, leaving implicit the “system” reference. Repeating myself, because it is just so important: a system in thermal equilibrium with its environment does not seek to maximize its own entropy, but instead changes to maximize the universe’s entropy; or equivalently — as is the main point here — changes to minimize its Helmholtz free energy.

23.2 Gibbs free energy and the phase transitions of pure substances (SITP 5.4)

- the **Gibbs free energy**

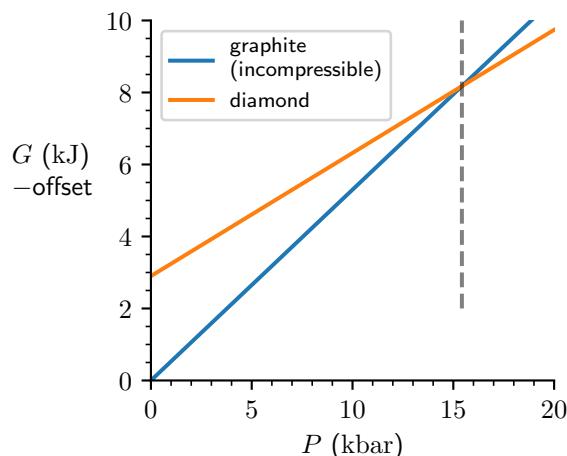
$$G := U + PV - TS \quad (345)$$

is simply an extension of the basic idea of the Helmholtz free energy in the case that the system is not confined to within a fixed volume, but rather is constrained by the constant pressure of a surrounding environment:

a system in thermal and mechanical equilibrium with its environment (at a specific temperature and pressure), will tend to *minimize* its Gibbs free energy, so as to *maximize* the entropy of the universe.

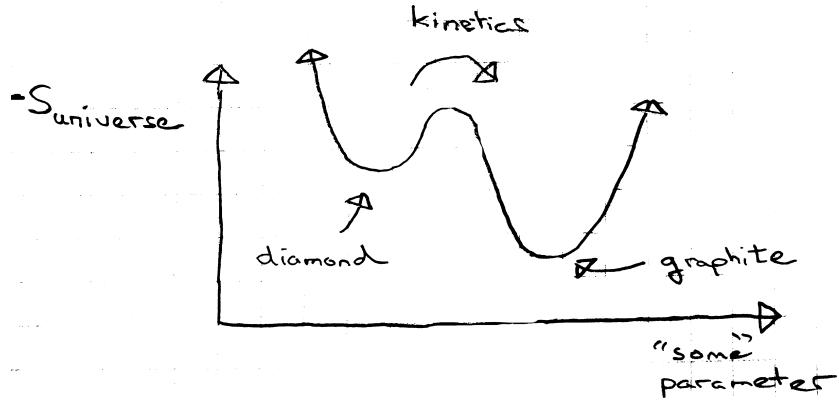
This interpretation of the Gibbs free energy is particularly useful for understanding phase transitions: as we change the temperature and pressure of the environment surrounding a material, the favoured phase has the lowest Gibbs free energy (since being in that phase will maximize the entropy of the universe). As a corollary: on a phase boundary, when two phases may coexist (e.g., ice and liquid water) the Gibbs free energies of the two phases are equal. The Gibbs free energy is the key to mapping out the phase boundaries in phase diagrams, such as that for the example of N₂ given in Fig. 15.

- as an example (from SITP), let us consider two phases of elemental carbon: diamond and graphite, at room temperature, but varying pressure. The 2nd law favours graphite at low pressures and diamond at high pressures, as the Gibbs free energy shows:



Gibbs free energy of graphite and diamond as a function of pressure, at room temperature. How to compute these lines will be discussed shortly. (After Fig 5.15 of D. V. Schroeder, *An introduction to thermal physics* (Addison Wesley, San Francisco, CA, 2000))

- but if graphite is favoured by thermodynamics, why may we observe both graphite *and* diamonds under normal atmospheric pressures? The reason is that despite a particular phase not being thermodynamically favoured, it can in fact be **metastable**. In a *highly schematic representation* (note the negative sign):



So although the transition to graphite is thermodynamically favoured (lower G , corresponding to a higher entropy of the universe) there is an intermediate highly unfavoured condition blocking rapid passage.

The metastability of diamond illustrates a point in the [introduction of Part III](#): thermodynamics rules out some processes from occurring, but it doesn't guarantee that a given process *will* happen, at least at any appreciable speed. Rates are a matter of what is known as **kinetics**, and not formally part of thermodynamics. This is similar to [heat flow](#); thermodynamics just tells us the conditions required for heat flow (hot to cold), not the rate at which it occurs (e.g., Fourier's law).

- for the reverse, more lucrative process — creating diamonds from graphite — thermodynamics provides us with necessary, but not sufficient conditions; i.e., a pressure of ≈ 15 kbar that appears in [this figure](#).

Let's quickly look at how we might estimate this pressure, given

- $\Delta G \approx 2.9 \text{ kJ}$, and
- $\Delta V \approx -1.88 \times 10^{-6} \text{ m}^3$

for the differences between the diamond and carbon phases of 1 mol of carbon at room temperature and pressure, as per the [physical reference data](#).

Recalling Eq. 390:

$$V = \left(\frac{\partial G}{\partial P} \right)_{T,N} \quad (346)$$

we may estimate that for constant temperature:⁸²

$$\Delta G(P) \approx \Delta G(P_0) + \Delta V \times (P - P_0) \quad (347)$$

where $P_0 = 1$ bar. Setting $\Delta G(P) = 0$, and rearranging to solve for $P - P_0$ gives:

$$P - P_0 \approx -\frac{\Delta G(P_0)}{\Delta V} \quad (348)$$

$$\approx -\frac{2.9 \times 10^3 \text{ J}}{-1.88 \times 10^{-6} \text{ m}^3} \quad (349)$$

$$\approx 1.5 \times 10^9 \text{ Pa} \quad (350)$$

$$\approx 15 \text{ kbar} \quad (351)$$

in agreement with [this plot](#). However, in practice for the artificial synthesis of diamond, reasonable kinetics requires $T \approx 1800$ K and $P \approx 15$ kbar.

- From the [physical reference data](#), the entropies of the graphite and diamond phases are:

$$\begin{aligned} S(\text{graphite}) &= 5.74 \text{ J/K} \\ S(\text{diamond}) &= 2.38 \text{ J/K} \end{aligned}$$

for 1 mol. A quick question to test your understanding (Problem 5.26 of SITP): Why is the graphite phase favoured at room temperature and pressure, despite the diamond phase having lower entropy?



⁸²We are making the dubious assumption that the volumes of diamond and graphite remain constant with increasing pressure. A more accurate approach is the subject of Problem 5.27 of SITP.

23.3 The Clausius-Clapeyron relation (SITP 5.3)

- we have just seen that for a specific temperature and pressure, the second law dictates that the phase with the lowest Gibbs free energy is favoured (more stable) over other phases.
- phase diagrams (such as Fig. 15) show the regions of pressure and temperature for which certain phases are more stable. How can we compute the lines that separate these regions (the **phase boundaries**)?
- on a phase boundary we expect the Gibbs free energies for two different phases to be equal:

$$G_1(P, T, N) = G_2(P, T, N). \quad (352)$$

This equation defines the phase boundaries; i.e. if we set T , we can compute the corresponding P that satisfies this equality. By varying T and computing the corresponding P 's we may map out the line on the phase diagram separating the two phases.

- to make direct use of Eq. 352 to determine phase boundaries we need to know the Gibbs free energies as a function of T and P . These are not always available. However as will now be shown, we may use Eq. 352 to derive an expression for dP/dT along phase boundaries in terms of two commonly known properties: the latent heat of the transition and the volume change between the phases.
- consider the *total* derivative with respect to T of both sides of Eq. 352 as we move along a phase boundary. We will keep the number of particles in each phase constant (N is always held constant in what follows). i.e. if $G_1 = G_2$ along the phase boundary then their total derivatives with respect to either T or P should also be equal.
- we will consider P as a function of T as we move along a phase boundary, so that the Gibbs free energy of each phase can be written as: $G_i(P(T), T, N)$. This makes it straightforward to see that

$$\frac{dG_i(P(T), T, N)}{dT} = \left(\frac{\partial G_i}{\partial P} \right)_T \frac{dP}{dT} + \left(\frac{\partial G_i}{\partial T} \right)_P. \quad (353)$$

From $dG = VdP - SdT + \mu dN$ we have:

$$\frac{dG_i(P(T), T, N)}{dT} = V_i \frac{dP}{dT} - S_i. \quad (354)$$

Equating this derivative for the two phases on either side of the phase line yields:

$$V_1 \frac{dP}{dT} - S_1 = V_2 \frac{dP}{dT} - S_2. \quad (355)$$

Rearranging gives:

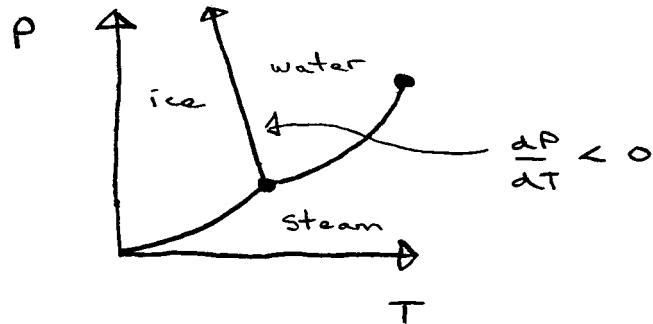
$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1}. \quad (356)$$

The difference in the entropies for the two phases is directly related to the latent heat of the phase transition. Specifically, recall that $L_{1 \rightarrow 2} := H_2 - H_1$ (Eq. 87). If the phase transition

takes place at constant temperature and pressure, by $dH = TdS - VdP + \mu dN$, we have $L_{1 \rightarrow 2} = H_2 - H_1 = T(S_2 - S_1)$, allowing us to write the **Clausius-Clapeyron relation**:

$$\boxed{\frac{dP}{dT} = \frac{L_{1 \rightarrow 2}}{T(V_2 - V_1)}} \quad (357)$$

- the Clausius-Clapeyron relation says something interesting about the melting of ice: Consider melting ice (phase 1) to make water (phase 2). For $1 \rightarrow 2$, $L > 0$ (i.e. we need to put heat into the system to melt ice), but $V_2 < V_1$ (water has a higher density than ice). The Clausius-Clapeyron relation tells us that for the phase boundary between ice and water: $dP/dT < 0$. This is consistent with the phase diagram:



- the depression of the melting point temperature of ice under increased pressure is sometimes offered as an explanation for the low friction of ice skates. However, as Problem 5.32 of SITP indicates, quantitatively assessing the validity of this claim is not straightforward. See however: <https://youtu.be/gM3zP72-rJE>
- normally solids are more dense than liquids and thus if $L_{\text{melting}} > 0$, the Clausius-Clapeyron relation tells us that $dP/dT > 0$. An interesting exception is the subject of SITP's Problem 5.34.

24 The available work interpretation of Helmholtz and Gibbs free energies (SITP 5.1 and 5.2)

24.1 Introduction

- remember that we defined the enthalpy as (Eq. 88)

$$H := U + PV \quad (358)$$

and it was useful for computing heat flow under constant pressure conditions *when only expansion/compression work is done*. But we could also interpret enthalpy as being

the amount of energy required to make a system U , and make room for it in a surrounding constant pressure environment PV .

- now we will consider analogous interpretations of our two new additional **thermodynamic potentials**:

$$F := U - TS \quad \text{the Helmholtz free energy} \quad (359)$$

$$G := U - TS + PV \quad \text{the Gibbs free energy} \quad (360)$$

- the Helmholtz free energy⁸³ F is the amount of energy that we need to create a system “minus” the energy that we can get for “free” from a surrounding bath at temperature T , in a manner that is consistent with the 2nd law. Specifically, we require:

$$S_{\text{system}} + \Delta S_{\text{bath}} \geq 0 \quad (361)$$

$$S_{\text{system}} - \frac{Q}{T} \geq 0 \quad (362)$$

where +ve Q corresponds to *into* system⁸⁴ and *out of* bath, so that the maximum amount of energy that may be extracted out of bath to help make the system is bounded:

$$Q \leq TS, \quad (363)$$

motivating the definition of F . i.e., if we take the energy $Q = TS$ from the bath to help create the system, we must still supply an additional $F = U - TS$ energy to create the system.

- Gibbs free energy is a combination of the concepts of enthalpy and Helmholtz free energy. It’s the energy that we must use to make a system U , minus the maximum amount that we can get from a surrounding constant temperature bath TS , plus the energy that is required to make room for it in a surrounding constant pressure environment PV .
- the preceding direct physical interpretations are appealing, but not terribly useful. They are not the reason these potentials were introduced. Instead — like for enthalpy — we make use of the *changes* ΔG and ΔF for processes. What do these changes tell us?
- for the change of a system, that is at the same temperature before and after (process is not required to be quasi-static):

$$\begin{aligned} \Delta F &= \Delta U - T\Delta S \\ &= Q + W - T\Delta S. \end{aligned} \quad (364)$$

Now apply the 2nd law:

$$\Delta S - \frac{Q}{T} \geq 0 \quad (365)$$

$$T\Delta S - Q \geq 0. \quad (366)$$

⁸³The symbol A is often used to represent the Helmholtz free energy, instead of F . In some older but classic references, such as G. N. Lewis et al., *Thermodynamics*, Rev. 2nd ed. (McGraw-Hill, New York, NY, 1961) (originally published in 1923), the symbol A is used for what we call F and the symbol F is used for what we call G . I mention these different conventions as a caution: always check definitions in sources.

⁸⁴We are now — after studying cyclic heat engines and refrigerators — back to the convention that positive Q and positive W refer to heat and work flowing *into* a system, unless explicitly indicated otherwise.

We may substitute for Q with a rearrangement of Eq. 364, yielding:

$$T\Delta S - (\Delta F - W + T\Delta S) \geq 0 \quad (367)$$

Simplifying gives:

$$-\Delta F + W \geq 0. \quad (368)$$

Equivalently:

$$W \geq \Delta F. \quad (369)$$

In words: $\Delta F = F_{\text{after}} - F_{\text{before}}$ tells us the *minimum* amount of *total* work that must be done on a system in thermal contact with a constant T bath.

- sometimes it is convenient to reexpress this constraint in an equivalent way: multiply both sides of Eq. 369 by -1 , reversing the inequality to obtain:

$$-W \leq -\Delta F \quad (370)$$

with the alternate — but equivalent — interpretation that $-\Delta F$ is the maximum amount of work that can be done *by* the system.

- what about ΔG ? Consider a process occurring while in equilibrium with a surrounding constant T , constant P environment. With the same T and P at the start and end of the process:

$$\Delta G = \Delta U - T\Delta S + P\Delta V \quad (371)$$

$$= Q + W - T\Delta S + P\Delta V \quad (372)$$

We have $W_{\text{mech}} = -P\Delta V$, so let us define:

$$W_{\text{other}} := W - W_{\text{mech}} \quad (373)$$

so that

$$\Delta G = Q + W_{\text{other}} - T\Delta S. \quad (374)$$

- what does the 2nd law tell us?

$$\Delta S - \frac{Q}{T} \geq 0, \quad (375)$$

or

$$T\Delta S - Q \geq 0. \quad (376)$$

Rearranging Eq. 374 to give Q , we have

$$T\Delta S - (\Delta G - W_{\text{other}} + T\Delta S) \geq 0 \quad (377)$$

$$-\Delta G + W_{\text{other}} \geq 0 \quad (378)$$

$$W_{\text{other}} \geq \Delta G \quad (379)$$

In words: ΔG tells us the minimum amount of additional non-mechanical work that we must do *on* a system (with temperature and pressure the same at both start and end of process).

- in many cases ΔG is negative, and it is useful to rewrite Eq. 379 in the equivalent form

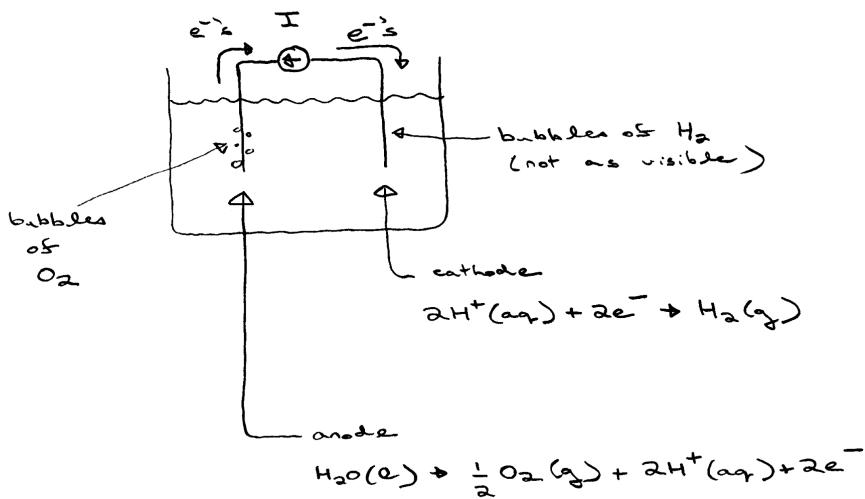
$$-W_{\text{other}} \leq -\Delta G \quad (380)$$

and interpret $-\Delta G$ as the *maximum* amount of non-mechanical work that can be done by a system.

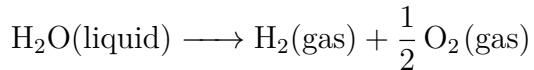
- so far we have not discussed any specifics of what the “other” in W_{other} refers to. One possibility is **electrical work**, as discussed in the following example.

24.2 Electrolysis of water (SITP 5.1)

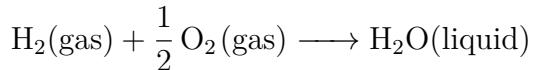
- passing an electrical current through water generates hydrogen and oxygen gas (the **electrolysis**⁸⁵ of water):



corresponding to the *net* reaction:



- what is the *minimum* amount of electrical work that must be done to break up 1 mol of H_2O (at 300 K, 1 bar)?
- the **reference data section** of SITP gives the standard **Gibbs free energies of formation** of various compounds. The usage of these is quite similar to that of standard enthalpies of formation, as described in Section 10.2.
- for 1 mol of liquid water, we find $\Delta_f G = -237 \text{ kJ}$, representing the change in Gibbs free energy of the system (products – reactants), when liquid water is formed from its elemental constituents in their most stable state. i.e., the change in Gibbs free energy for the reaction:



⁸⁵More generally, the term electrolysis refers to the passage of electrical current through a liquid to produce a chemical reaction at the electrodes (source: OED). The industrial production of Aluminum relies on electrolysis of solutions of molten salts (Hall-Héroult process.)

and thus for the reverse reaction, the electrolysis of a mol of water, we require a minimum of $\Delta_f G = 237 \text{ kJ}$ of electrical work to be done *on* the system.

- the opposite reaction is also possible: we can extract a *maximum* of 237 kJ of electrical work in a **fuel-cell** device (i.e., “hydrogen” power). In some sense, we might consider the efficiency of such a hydrogen fuel cell device to be:

$$\frac{\Delta G}{\Delta H} \approx \frac{237}{286} \quad (381)$$

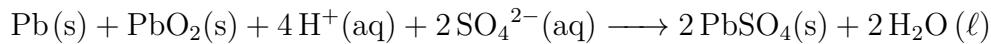
$$\approx 0.83 \quad (382)$$

which is much higher than would normally be achieved by a heat engine; e.g., with a cold reservoir of 300 K, we would need $T_H \approx 1800 \text{ K}$ to achieve $e = 0.83$ with a Carnot engine.

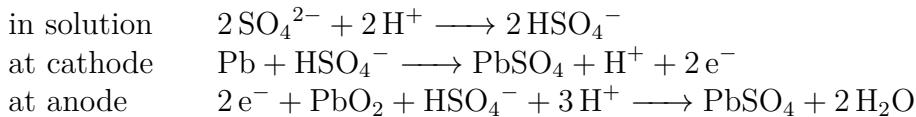
- in other words, it is much better to try to extract work directly from a reaction as opposed to using that same reaction to provide the heat for a heat engine. Maybe we will eventually view heat engines as a primitive tool of early humankind.
- as Section 21 suggested, biology seems to have rejected the heat engine. For more details, now that we know about the Gibbs free energy, see: [Problem 5.6 from SITP, Muscles as fuel cells](#) and [Problem 5.7 from SITP, Muscle efficiency](#).

24.3 Lead acid batteries (SITP 5.1)

- as a second example of the usage of Gibb’s free energies, let us consider the reaction that occurs in the lead acid batteries used to start most internal combustion automobiles:



This reaction may be thought of as consisting of the steps:



The electrons flow through an external circuit, and this external circuit allows electrical work to be extracted from the reaction (the chemical potential terms).

- computing ΔG is now a bit more involved. Using the analogy to Hess’ law:

$$\begin{aligned}
 \Delta G &= \text{products} - \text{reactants} \\
 &= 2 \times \Delta_f G(\text{H}_2\text{O}(\ell)) + 2 \times \Delta_f G(\text{PbSO}_4(\text{s})) \\
 &\quad - [\Delta_f G(\text{Pb(s)}) + \Delta_f G(\text{PbO}_2(\text{s})) + 4 \times \Delta_f G(\text{H}^+(\text{aq})) + 2 \times \Delta_f G(\text{SO}_4^{2-}(\text{aq}))] \\
 &= 2 \times (-273.13 \text{ kJ}) + 2 \times (-813 \text{ kJ}) \\
 &\quad - [0 \text{ kJ} + -217.33 \text{ kJ} + 4 \times (0 \text{ kJ}) + 2 \times (-744.53 \text{ kJ})] \\
 &= -393.9 \text{ kJ}
 \end{aligned} \quad (383)$$

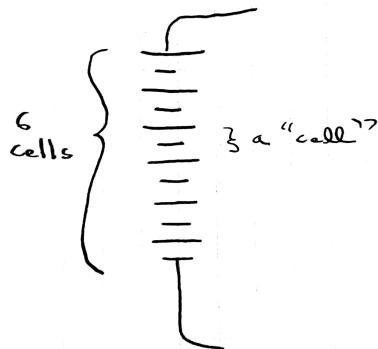
- what should we compare this number to? For this, we ask the maximum amount of work might be done *per unit charge*. Note that two electrons flow through the external circuit (for -393.9 kJ) so that:

$$\frac{-W}{Q} \approx \frac{393.9 \text{ kJ}}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{23}} \quad (384)$$

$$\approx 2.04 \frac{\text{J}}{\text{C}}. \quad (385)$$

But the units of J/C are more commonly referred to as **Volt** (V).

Now the numerical value of ΔG is more tangible. A car battery consists of 6 cells in series, giving a total voltage of $6 \times 2 \text{ V} = 12 \text{ V}$.



25 Thermodynamic potentials — general considerations

25.1 Thermodynamic identities

- the thermodynamic potentials H , F , and G , have been introduced in a manner which emphasizes their individual specific uses. Now we will take a step back and consider the features that these potentials have in common. For uniformity, we consider the internal energy U to be a “potential” as well.⁸⁶
- we will first consider the consequences that these potentials exist at all (under equilibrium conditions).
- in Part II of the notes we showed that computing expressions for the multiplicity (and thus entropy) of a system as a function of volume and entropy enabled computation of its temperature and pressure. Barring any problems with uniqueness, $S(U, V, N)$ can be rearranged to give U as function of S and V ; i.e., $U(S, V, N)$, which we now also consider to be a thermodynamic potential in addition to H , F , and G . We may not know the explicit form of this function — it may be difficult to compute or measure, but we may be confident that it *does* exist.

⁸⁶Note that the “thermodynamic potentials” differ from the normal potentials of classical mechanics. For example, U includes any *kinetic energy*. Same word — distinct entities.

- earlier (Eq. 233), when introducing the chemical potential, we wrote

$$dU = TdS - PdV + \mu dN, \quad (386)$$

valid for a system of a single particle type. This equation is known as the **thermodynamic identity**, possibly setting some sort of Olympic-like record for generic and vague naming. Recalling the interpretation of these “isolated differentials” given in footnote 27, let us first consider a “path” in which V and N are fixed and S is varied, so that the last two terms are zero, and thus

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N}. \quad (387)$$

Likewise, if we consider a path in which S and N are fixed and V is varied:

$$P = - \left(\frac{\partial U}{\partial V} \right)_{S,N} \quad (388)$$

from which, in Section 15.2, we “derived” the ideal gas law, given the Sackur-Tetrode expression for S as a function of U , N , and V .

Turning from U to G , and writing $dG = dU + d(PV) - d(TS) = dU + VdP + PdV - TdS - SdT$ and combining with Eq. 386, we have a second “thermodynamic identity”:

$$dG = VdP - SdT + \mu dN, \quad (389)$$

from which we can deduce (in a similar manner to Eq.’s 387 and 388 for T and P) that

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P,N} \quad V = \left(\frac{\partial G}{\partial P} \right)_{T,N} \quad \text{and} \quad \mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}. \quad (390)$$

- these relationships are useful for estimating how G changes with temperature and pressure.

Example: SITP Problem 5.10

Analogous relationships may be derived from the thermodynamic identities associated with “ dH ” and “ dF ”.

- for each of the thermodynamic potentials, the corresponding thermodynamic identity points to the primacy of a particular set of variables for that potential. For U , the variables are S and V . For G , the variables are P and T , and so-on for F and H . We will refer to these as the **natural variables** for each potential.⁸⁷

⁸⁷The relationship between the various potentials and their associated natural variables can be formalized using the Legendre transformation concept — which is probably more familiar to most physics students in the context of classical mechanics i.e., the transformation from Lagrangians to Hamiltonians. See, for example, R. K. P. Zia et al., “Making sense of the Legendre transform”, *American Journal of Physics* **77**, 614–622 (2009).

25.2 Maxwell's relations

- let us return to the “fundamental” thermodynamic identity (Eq. 386) and the corresponding expressions for T and P given by Eq.’s 387 and 388. Assume that N is fixed, so that U may be considered solely as a function of its two natural variables S and V . That U exists at all has some nice consequences, similar in a *vague* sort of way to the fact that some forces (conservative) are derivable from potentials in mechanics.

Suppose that we were to differentiate the expression for T given in Eq. 387 with respect to V while holding S constant, and also differentiate the expression for P given by Eq. with respect to S while holding V constant. In the terminology of mathematics, we are computing the 2nd order mixed partial derivatives:

$$\frac{\partial}{\partial x} \frac{\partial}{\partial y} f(x, y) \quad \text{and} \quad \frac{\partial}{\partial y} \frac{\partial}{\partial x} f(x, y) \quad (391)$$

of a function of two variables $f(x, y)$. But for well-behaved functions these two derivatives are in fact **equal**.

Returning to “physics variables”, this equality of 2nd order mixed partial derivatives becomes:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V, \quad (392)$$

a useful non-trivial relation that — from the preceding derivation — we may consider a consequence of the existence of the thermodynamic potential $U(S, V, N)$. It is one of **Maxwell’s relations**. Similar contrivances involving the three other common thermodynamic potentials H , F and G , yield three more of these Maxwell’s relations. (See also SITP Problem 5.12.)

- Maxwell’s relations are surprisingly useful for deriving relationships between thermodynamic quantities. The next section gives the canonical example: the general relationship between C_P and C_V .

25.3 The general relationship between the constant pressure and constant volume heat capacities

- the relationship $C_P - C_V = Nk$ for ideal gases (Eq. 47), is useful in adiabatic expansion and compression problems, particularly when accompanied by the additional assumption that the heat capacities are temperature independent. However our justification of this expression for $C_P - C_V$ (in Section 6) was based on Joule’s experiment which indicated that for an ideal gas the energy per molecule *only* depends on the temperature and type of molecules.

We are now in the position to show that $C_P - C_V = Nk$ is a direct consequence of the ideal gas law ($PV = nkT$). Furthermore, we will find the $C_P - C_V$ for *any* material — not just ideal gases — can be expressed in terms of its isobaric thermal expansivity and isothermal compressibility — two quantities which are relatively straightforward to measure.

- we start from the definitions of C_P and C_V :

$$C_P - C_V = \left(\frac{\partial H}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V \quad (393)$$

$$= \left(\frac{\partial(U + PV)}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V \quad (394)$$

$$= \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V. \quad (395)$$

Now consider U as a function of T and V :

$$C_P - C_V = \left(\frac{\partial U(T, V)}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V. \quad (396)$$

$$= \left(\frac{\partial U}{\partial T} \right)_V + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V. \quad (397)$$

$$= \left(\left(\frac{\partial U}{\partial V} \right)_T + P \right) \left(\frac{\partial V}{\partial T} \right)_P \quad (398)$$

Now let us consider U as a function of its natural variables S and V , so that

$$\left(\frac{\partial U}{\partial V} \right)_T = \left(\frac{\partial U(S, V)}{\partial V} \right)_T \quad (399)$$

$$= \left(\frac{\partial U}{\partial V} \right)_S + \left(\frac{\partial U}{\partial S} \right)_V \left(\frac{\partial S}{\partial V} \right)_T \quad (400)$$

$$= -P + T \left(\frac{\partial S}{\partial V} \right)_T \quad (401)$$

Substituting this into Eq. 398 gives:

$$C_P - C_V = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P. \quad (402)$$

Now we need a Maxwell relation

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (403)$$

derived from the thermodynamic identity associated with dF . Using this relation in Eq. 402 gives:

$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P. \quad (404)$$

and using a triple product identity (see Appendix A) to replace $(\partial P / \partial T)_V$ gives:

$$C_P - C_V = -T \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial V}{\partial T} \right)_P \quad (405)$$

Recall the definition of the isobaric expansivity:

$$\beta := \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (406)$$

and isothermal compressibility

$$\kappa_T := -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (407)$$

so that Eq. 405 may be condensed to:

$$C_P - C_V = \frac{TV\beta^2}{\kappa_T}$$

(408)

Some points about this result:

- the expression is consistent with $C_P - C_V$ being extensive, as it should be — a good check.
- the equation of state for an ideal gas can be used to evaluate the RHS (Eq. 408), showing Mayer's relationship $C_P - C_V = Nk$ for an ideal gas. Recall that when we first justified this relationship (in Section 6) we relied on Joule's empirical observations. We now know Mayer's relationship to be a logical consequence of the ideal gas law.
- examination of the derivation shows the usage of a number of elementary, but fundamental, mathematical tools typical of macroscopic thermodynamics: change of variables, triple product rule, and Maxwell's relations.
- as Problem 1.46 of SITP illustrates, directly measuring C_V for solids and liquids is usually difficult because of the high pressures required to confine the sample to within a fixed volume. Instead C_P is measured. Since both β and κ_T are normally straightforward to measure, Eq. 408, allows C_V to be determined, even though it can not be directly measured.
- In Problem 5.14 of SITP, it is suggested that $C_P - C_V$ be evaluated for liquid water and mercury (under “standard” conditions, $T \approx 300$ K, $P \approx 1$ bar). I have also considered solid copper.⁸⁸ For 1 mol of each I find:

material	β (K ⁻¹)	κ_T (Pa ⁻¹)	V (m ³)	$C_P - C_V$ (J/K)	C_P (J/K)	$\frac{C_P - C_V}{C_P}$
water	2.57×10^{-4}	4.52×10^{-10}	18.068×10^{-6}	0.79	75.29	0.010
mercury	1.81×10^{-4}	4.04×10^{-11}	14.81×10^{-6}	3.6	27.98	0.13
copper	5.0×10^{-5}	7.9×10^{-12}	7.06×10^{-6}	0.7	24.5	0.029

⁸⁸For copper, I have used the data from M. W. Zemansky, *Heat and thermodynamics; an intermediate textbook*, 5th edition (McGraw-Hill, New York, 1968). The temperature dependence of $C_P - C_V$ is shown on page 322 of this reference.

Previously — in footnote 44 — I remarked on the absence of the concept of volume or pressure in the Einstein solid model. We simply referred to the unqualified “heat capacity”. Here we see, at least for copper, that ignoring the difference between C_P and C_V is not too horrible, at least in comparison to a noble gas at room temperature, for which $(C_P - C_V)/C_P \approx 0.4$.

- I must admit that derivations like the one just given for $C_P - C_V$ often involve a bit of trial and error and it is easy to get lost in the land of partial derivatives. Please accept this complementary [map](#).

26 Macroscopic closing words

We have now covered the fundamentals of macroscopic thermodynamics. Of course, fluency requires practice in the application of these principles. Fortunately, interesting applications of thermodynamic principles are abundant.⁸⁹

Much of what you have learned here will be enhanced and extended by your future study of statistical mechanics, the subject matter of Phys 359, *Statistical Mechanics*. This is an enormous, fascinating area of physics, filled with mathematical, computational, and experimental challenges. Part II has given you a reasonable idea about the nature of statistical mechanics.

As final words for what is normally the end of Phys 358, I would like to provide my personal answer to the question: what should one remember about macroscopic thermodynamics once the proverbial “dust has settled”? Or more concretely: once the lectures, problem sets, tests, and so-on are done? Most of us are going to be have to be selective in how we organize the residues of the subject in our minds. For me, I think it is the concept of the *Helmholtz free energy* that is critical. I want to remember what it is, and how has been defined in a way to be useful — not especially the available work interpretation, but instead the relationship between a system’s free energy and the maximization of the universe’s entropy. Being able to state all of this in my own words, understand the underlying principles (including entropy, the second law, etc...), provide examples, and so-on, is what *I* choose to boil the essence of this subject down to. It organizes all of what is most important about thermodynamics *to me*. Again, in the spirit of Maxwell’s attitude, as mentioned in the [Introduction](#), I wish you success in your own condensation!

⁸⁹For practice in the application of the basic principles of thermodynamics, I recommend the remaining sections of Chapter 5 of SITP: “5.4 Phase transformation of mixtures”, “5.5 Dilute solutions”, and “5.6 Chemical equilibrium”. I regret that there is not enough time to cover this material during Phys 358. If you self-study these areas in the future, please do get in contact with me for discussions and/or help.

Part IV

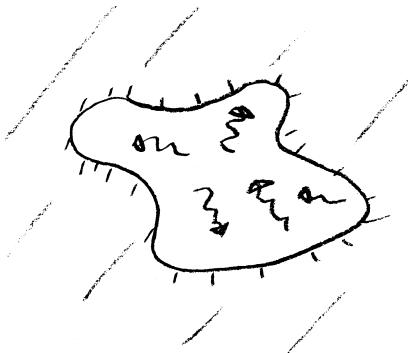
Thermal radiation and the temperature of the earth

27 Introduction

- we have all felt the “warmth” of a glowing fire. In addition to conduction and convection, electromagnetic waves (a type of radiation) may transport energy between objects at different temperatures. This **thermal radiation** is critical to understanding the temperature of the earth.
- this is the final part of these notes, making use of much of the material that we have studied so far. It will also give some insights into the historical development of quantum mechanics.⁹⁰

28 The thermodynamics of thermal radiation

- let us look at the details of thermal radiation, beginning with a model system:



A trapped **photon gas** within a cavity. The cavity walls are reflecting so that the radiation is trapped. Since photons are an inherently quantum mechanical concept, I will initially avoid the “photon gas” terminology, as I wish to be explicit about where the introduction of the ideas of quantum mechanics are required. So we begin by considering the radiation within the cavity to be classical i.e., described by Maxwell’s equations.

- assume that the radiation field in the cavity is in thermal equilibrium with the surrounding solid, so that they both have temperature T . You might (or should) be wondering: what does it mean for a radiation field to be at a certain temperature? Recall that the definition of temperature that we have adopted depends on defining the entropy and energy for a system. The energy associated with a given electromagnetic field configuration is well-defined.⁹¹ However, the reverse is not true. Specifically, the total electromagnetic energy *does not* uniquely define

⁹⁰This part of the notes is normally not part of UW Phys 358. However, it may serve as both a review, and a chance to “put into action” what you have learned in the previous parts. I very much welcome your comments and questions, even after the course is finished.

⁹¹The energy density of an electromagnetic field is given by:

$$u = \frac{1}{2} \left(\epsilon_0 E^2 + \frac{1}{\mu_0} B^2 \right). \quad \text{EM theory}$$

the electromagnetic fields within the cavity: different field configurations may have the same energy, giving rise to a multiplicity Ω . i.e., the number of microscopic states corresponding to a macrostate. Recall that entropy is $S = k \ln \Omega$. So that if given a certain cavity energy we know how “count” the number of contributing field configurations, we may determine temperature of the trapped radiation by $T := (\partial U / \partial S)_V$. Thus we see in principle — if not yet in practice — how the concept of temperature applies to a radiation field.

- the pressure of the radiation on the walls and the cavity electromagnetic energy density $u := U/V$ are related:

$$P = \frac{1}{3}u. \quad \text{EM theory} \quad (409)$$

This is a result of classical electromagnetic theory (i.e., does not require the concept of “photons” at all).⁹² In the SI system, the units of u are J/m^3 , which are also the units for pressure. (With the ideal gas law in the form $P = NkT/V$ it is clear that the RHS, and thus the LHS, may be written with units of J/m^3).

- empirically it is observed that if the cavity is large enough,⁹³ then u only depends the temperature of the surrounding material, so we write $u(T)$.
- given the relationship between P and $u(T)$ of Eq. 409, we can determine the temperature dependence of $u(T)$ using the following purely thermodynamic argument (straightforward, but lengthy — terminating at Eq. 424):

Consider the thermodynamic identity:

$$dU = TdS - PdV + \mu dN. \quad (410)$$

With the “photon” gas interpretation, N might refer to the number of photons trapped in the cavity. However, as photons may be readily created and destroyed (by energy exchange with the surrounding solid) it turns out that $\mu = 0$. Specifically, since $dF = -SdT - PdV + \mu dN$, we have

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V,T}. \quad (411)$$

At a given T , the number of photons in the cavity will adjust to minimize F , thereby maximizing the *total* entropy of the universe (see Section 5.2 of SITP). A condition for this maximum is (given a constant V and T):

$$\left(\frac{\partial F}{\partial N} \right)_{V,T} = 0 \quad (412)$$

See, for example, Eq. (8.5) on pg 357 of D. J. Griffiths, *Introduction to electrodynamics*, Fourth edition (Cambridge University Press, Cambridge, United Kingdom ; New York, NY, 2018). The total energy may be obtained by integrating u over the cavity volume.

⁹²I will use some results from classical electromagnetic theory and attach the label “EM theory”. Please see the discussion at the [end of this section](#).

⁹³To decide “how large” is large enough, we should compare the size of the cavity to the wavelengths of the thermal radiation. We will not discuss any further; a relevant reference is: H. P. Baltes, “Planck’s radiation law for finite cavities and related problems”, *Infrared Physics* **16**, 1–8 (1976).

leading us to conclude (from Eq. 411) that $\mu = 0$.

Now let's return to Eq. 410 with $\mu = 0$ and consider changing V while leaving T constant:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P. \quad (413)$$

Now we need a **Maxwell relation** (see Section 25.2). Start from

$$dF = -SdT - PdV \quad (414)$$

which tells us that

$$S = - \left(\frac{\partial F}{\partial T}\right)_V \quad (415)$$

and

$$P = - \left(\frac{\partial F}{\partial V}\right)_T \quad (416)$$

Since the order of partial derivatives doesn't matter,

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T}\right)_V\right)_T$$

or, in terms of P and S :

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \quad (417)$$

which is one of several of Maxwell's relations.

We can now rewrite Eq. 413 as

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P. \quad (418)$$

Substituting $U = u(T)V$ and $P = \frac{1}{3}u(T)$, we get

$$\frac{\partial}{\partial V} (u(T)V)_T = T \frac{\partial}{\partial T} \left(\frac{u(T)}{3}\right)_V - \frac{u(T)}{3}. \quad (419)$$

Rearrange to give:

$$u(T) = T \frac{1}{3} \frac{\partial}{\partial T} (u(T))_V - \frac{u(T)}{3}. \quad (420)$$

Since $u(T)$ does not depend on volume (it is an energy *density*), we have established a differential equation determining how $u(T)$ changes with temperature. With a slight rearrangement and simplification:

$$\frac{d u(T)}{dT} = 4 \frac{u(T)}{T}. \quad (421)$$

This equation can rearranged and integrated:

$$\int \frac{du(T)}{u(T)} = 4 \int \frac{dT}{T} \quad (422)$$

giving

$$\ln u(T) = 4 \ln T + \ln C, \quad (423)$$

where a constant of integration $=: \ln C$ has been introduced. Equivalently:

$$u(T) = CT^4. \quad (424)$$

Therefore the electromagnetic energy density in the cavity $u(T)$ is proportional to T^4 \square .

We will discuss the determination of C shortly.

- what is the frequency of this trapped electromagnetic radiation? To put it more crudely: does this radiation consist of gamma rays, x-rays, visible light, microwaves or radio-waves? We might suspect that there is some sort of mixture of these, for which we must specify the proportions.
- more precisely, we need a distribution function to describe how the electromagnetic energy density is distributed in frequency. Let us define a quantity $u_\nu(\nu, T)$ such that the electromagnetic energy density within a frequency range ν to $\nu + d\nu$ is $u_\nu(\nu, T)d\nu$, and thus

$$u(T) = \int_0^\infty u_\nu(\nu, T) d\nu. \quad (425)$$

- using electromagnetic theory and the T^4 temperature dependence of the energy density given by Eq. 424, Wien was able to show (in 1894) that the distribution of energy density over frequencies must be of the form:

$$u_\nu(\nu, T) = \nu^3 f(\nu/T), \quad \text{EM theory} \quad (426)$$

where f is a function of a single variable ν/T . This constraint on the form of u_ν became known as **Wien's displacement law** and simplified the problem of finding $u_\nu(\nu, T)$ to finding the function f .

- we can verify that Eq. 426 does in fact satisfy the T^4 constraint from Eq. 424. (Wien went in the opposite, more difficult direction.) In particular, if we substitute Wien's form for $u_\nu(\nu, T)$ given by Eq. 426 into Eq. 425:

$$u(T) = \int_0^\infty u_\nu(\nu, T) d\nu \quad (427)$$

$$= \int_0^\infty \nu^3 f(\nu/T) d\nu \quad (428)$$

To simplify, make a change of variables using $\theta := \nu/T$, and thus $d\theta = d\nu/T$, to obtain:

$$u(T) = \int_0^\infty \underbrace{(\theta T)^3}_{\nu^3} f(\theta) \underbrace{T d\theta}_{d\nu} \quad (429)$$

$$= T^4 \underbrace{\int_0^\infty \theta^3 f(\theta) d\theta}_{=:C}. \quad (430)$$

The integral on the right hand, denoted by C , is temperature independent — depending only on the function f . Thus we have recovered the T^4 temperature dependence of Eq. 424 with C given by the integral shown. (This will be useful once we have the function f .)

- in addition to Eq. 426, Wien also proposed a specific form for f :

$$f(\theta) = \frac{8\pi\alpha}{c^3} e^{-\beta\theta} \quad \text{wrong} \quad (431)$$

where c is the speed of light, and α and β are constants to be empirically determined from observations of the $u(\nu, T)$ that results from substitution of Eq. 431 into Eq. 426:

$$u_\nu(\nu, T) = \nu^3 \frac{8\pi\alpha}{c^3} e^{-\beta\nu/T}. \quad \text{wrong} \quad (432)$$

However, as we shall see, this specific form for f is not correct.

- how can we observe the spectral distribution of cavity radiation u_ν to check Wien's proposed f ? Perhaps we could cut a hole in the side of the box to let the photon gas escape, being careful to make sure that the escaping photon gas was being “replenished” through the surrounding walls at a sufficient rate so that the cavity radiation could be considered to be at a constant temperature (at least approximately). We could then “disperse” the emitted radiation to observe a spectrum which could then be related back to $u_\nu(\nu, T)$. In the next section, we will look at this quantitatively. For now we will just assume that these measurements allow determination of u_ν within the cavity.
- Lummer and Pringsheim's measurements of u_ν were critical in showing that Wien's form for f (Eq. (431)) was not correct:

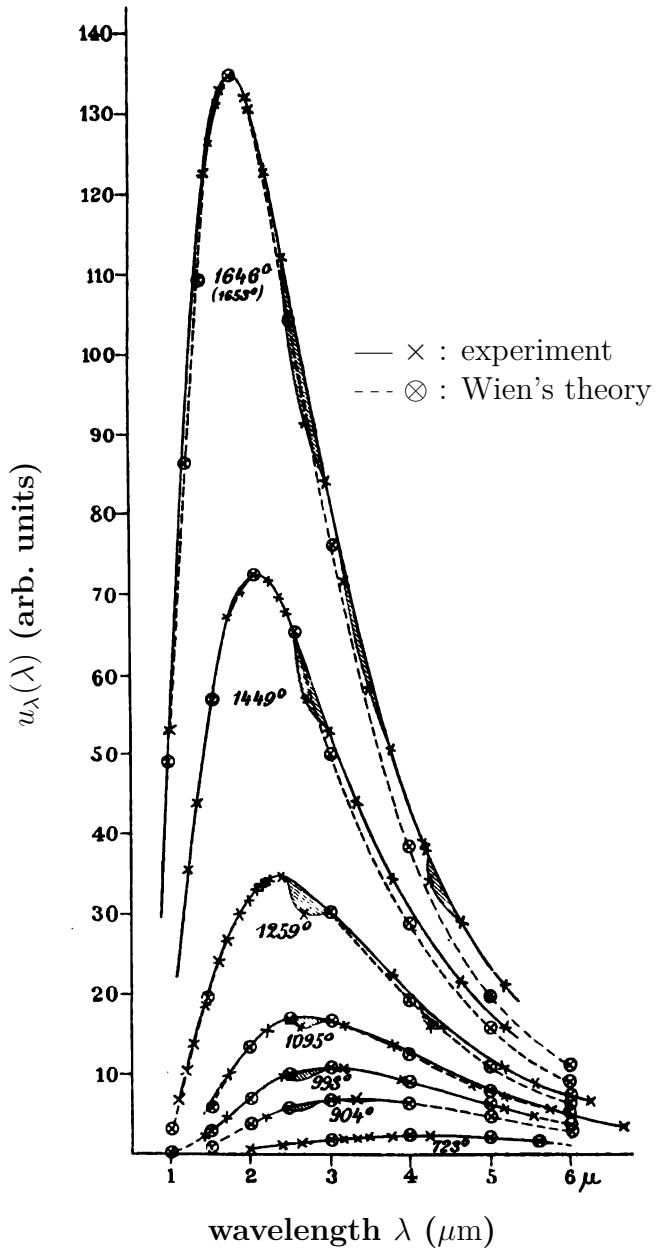
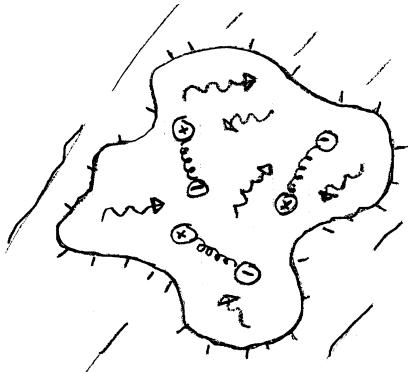


Figure 19: Lummer and Pringsheim's experimental observations of the thermal radiation emitted from a cavity at different temperatures. The indicated temperatures are in Kelvin. The vertical axis is proportional to the energy per unit wavelength, not frequency. The shaded areas indicate atmospheric absorption due to water and carbon dioxide between the cavity and the detector. Wien's theory (Eq. 426) is given by the dashed lines and systematically deviates from the data at long wavelengths (low frequencies). Source: Lummer and Pringsheim's original work (Verhandlungen der Deutschen Physikalischen Gesellschaft, November 1899, pg 215, in German, <https://archive.org/details/verhandlungende63unkngoog>).

- guided by this discrepancy⁹⁴ Planck found the correct f and his successful solution initiated the quantum mechanical revolution. I will not do justice to his struggles, but instead, outline in the broadest terms the physics involved, with a hope to motivating you to study some of the issues in more complete detail.
- Planck's original approach was to try to find some simple formula for f that agreed with the experimental data. He succeeded and then pursued an explanation for the specific form of f that he found. His theoretical model consisted of a set of simple harmonic oscillators within

⁹⁴Many short accounts of Planck's work minimize the guiding role of experimental observations by Lummer, Pringsheim, Rubens and Kurlbaum. One that does not is: M. Nauenberg, "Max Planck and the birth of the quantum hypothesis", *American Journal of Physics* **84**, 709–720 (2016)

the cavity, coupled to its electromagnetic field. These harmonic oscillators have resonance frequencies distributed over all frequencies and are in thermal equilibrium (have the same T as the cavity radiation):



- from electromagnetism it is possible to show that

$$u_\nu(\nu, T) = \frac{8\pi\nu^2}{c^3} \langle E(\nu, T) \rangle \quad \text{EM theory} \quad (433)$$

where $\langle E(\nu, T) \rangle$ is the average energy of *each* one-dimensional oscillator of frequency ν .

- the equipartition theorem tells us that each one-dimensional oscillator has two “quadratic-like” degrees of freedom contributing to its energy ($p^2/2m + kx^2/2$) and thus, if Eq. 1.23 of SITP ($U_{\text{thermal}} = Nf\frac{1}{2}kT$) is applicable, then the average energy of a single oscillator is $\langle E(\nu, T) \rangle = kT$.

$$u_\nu(\nu, T) = \frac{8\pi\nu^2}{c^3} kT, \quad \text{wrong} \quad (434)$$

a result that is consistent with Wien’s general form (Eq. 426), and has come to be known as the **Rayleigh-Jeans law**.⁹⁵ (Yes, in correspondence with anthropomorphic equivalents, it is both a “law” and wrong!)

- the Rayleigh-Jeans law is in reasonable agreement with experimental observations of $u_\nu(\nu, T)$ at “low frequencies” (or long wavelengths).
- at this point you might be experiencing *deja vu*. This situation is quite similar to one encountered earlier in the course when we were studying the Einstein solid model. In particular, the Einstein solid model for heat capacities was consistent with the equipartition theorem (as used above to derive the Rayleigh-Jeans law) when kT was large compared to the oscillator quantization energy (ϵ in Problem 3.25 of SITP). Equivalently, the equipartition theorem is valid “at low oscillator quantization energies” (compared to kT), suggesting that perhaps

⁹⁵If you are interested in how physics history is told in textbooks, see: J. R. Persson, “Evolution of quasi-history of the Planck blackbody radiation equation in a physics textbook”, *Am. J. Phys.* **86**, 887–892 (2018). Persson points out that a succession of editions of a popular first-year textbook morphed the chronology of the thermal radiation formulae to make their development appear more logical. In particular, Eq. 434 was developed by Rayleigh (and refined by Jeans) in parallel with Planck’s work, not before it. Viewing Planck’s work as a correction or improvement of the results of the Rayleigh-Jeans formula (as I do here) *is* more logical, but doesn’t accurately reflect history.

there is a connection between the Einstein model and Planck's oscillators *if* we can connect the quantized oscillator energies of the Einstein model with the frequencies of thermal radiation.

- let us briefly recall some results of the Einstein model from Problem 3.25 of SITP. We start with an approximate expression for the multiplicity of an Einstein solid consisting of N oscillators and q energy units ($U = q\epsilon$):

$$\Omega(N, q) \approx \left(\frac{q+N}{q} \right)^q \left(\frac{q+N}{N} \right)^N. \quad (435)$$

valid for large q and N , but with no constraint on their relative magnitudes (i.e., neither the high- or low-temperature limiting cases). We then used $S := k \ln \Omega$, and $T = dU/dS$ to determine a relationship between U and T . We found:

$$U = \frac{N\epsilon}{e^{\epsilon/(kT)} - 1}. \quad (436)$$

At this point, we then looked at the heat capacity of this model ($C = dU/dT$), as that may be readily compared with experiment. Equation 436 implies an average energy per oscillator of:

$$\frac{U}{N} = \frac{\epsilon}{e^{\epsilon/(kT)} - 1}. \quad (437)$$

- Planck considered that there were many oscillators for each frequency ν , and that an oscillator of frequency ν could have energies 0, $h\nu$, $2h\nu$, ..., where h is a constant, so that

$$\langle E(\nu, T) \rangle = \frac{h\nu}{e^{h\nu/(kT)} - 1}. \quad (438)$$

- substitution of Eq. 438 into Eq. 433 gives **Planck's distribution**:

$$u_\nu(\nu, T) = \left(\frac{8\pi h\nu^3}{c^3} \right) \frac{1}{e^{h\nu/(kT)} - 1}.$$

(439)

Note that this form of u_ν obeys Wien's displacement law (Eq. 426), with

$$f(\theta) = \left(\frac{8\pi h}{c^3} \right) \frac{1}{e^{h\theta/k} - 1}. \quad (440)$$

As we have shown (Eq. 430), Wien's displacement law gives the T^4 dependence of energy density, that we initially justified using a thermodynamic argument. However, now we may determine the precisely known constant C , appearing in Eq. 424 using Eq. 430. Thus

$$u = \frac{8\pi^5 (kT)^4}{15(hc)^3}.$$

(441)

(BTW: it is useful to remember hc has dimensions of energy \times length, especially in relativistic quantum mechanics; here it makes it obvious that the dimensions of this equation are correct.)

- the distribution of Eq. 439 agreed much better with experiment than the *specific* form originally proposed by Wien (Eq. 431). See Fig.'s 20 and 21.

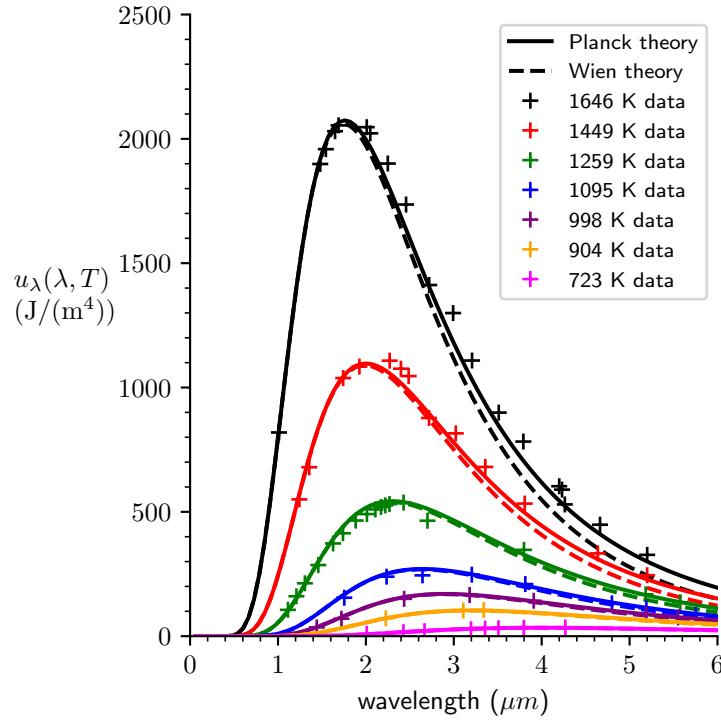


Figure 20: Comparison between Lummer and Pringsheim's observations (see Fig. 19) and the theories of Wien and Planck. Note that Wien's theory systematically underestimates u_λ at long wavelengths (low frequencies). Planck's theory is closer to the data, but also appears to underestimate at long wavelengths. The most convincing experimental evidence for Planck's theory is the data of Rubens and Kurlbaum (see Fig. 21).

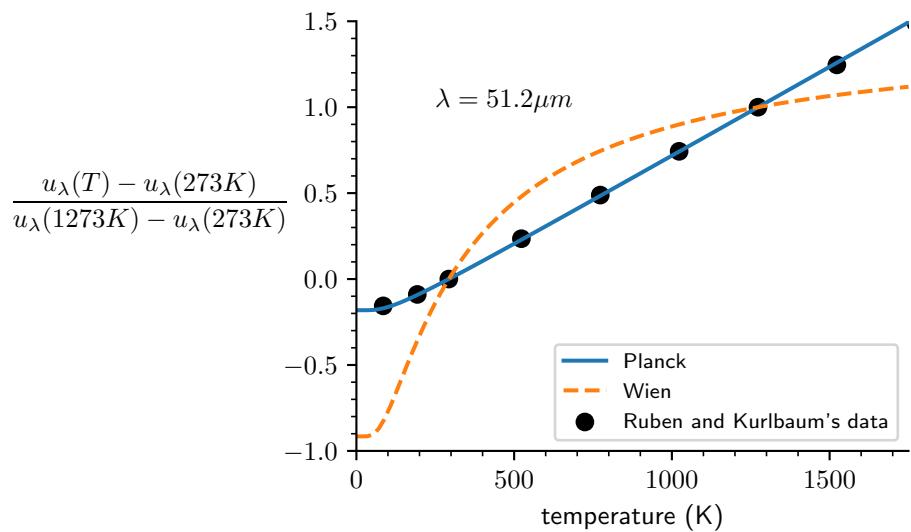


Figure 21: Comparison between Ruben and Kurlbaum's observations and the theories of Wien and Planck. The data and theories are constrained to agree at 293K and 1273K. This data provided strong evidence in favour of Planck's theory. Source of data: <https://ui.adsabs.harvard.edu/abs/1901ApJ....14..335R/abstract>

- Planck was uncomfortable with the introduction of the idea of quantizing the energy of the oscillators, as it didn't seem to have any physical motivation. We now know that this was the first step in the discovery of quantum mechanics and the constant h that he introduced is called Planck's constant in his honour. Einstein took the further, critical leap by eliminating the quantized material oscillators altogether, and proposing that *the electromagnetic field itself was quantized*. In short, the energy of a photon is

$$E = h\nu.$$

Einstein's viewpoint is the modern one and is exploited in Section 7.4 of SITP to derive Eq. 439 using more general methods (see the discussion immediately following SITP Eq. 7.79). The approach that I have presented here has the advantage that it offers some insight into the history of quantum mechanics, and it allows us to discuss thermal radiation prior to learning the general techniques of Chapter 6 and 7 of SITP (techniques that you will learn in Phys 359).

- a stringent “test” of the Planck formula (Eq. 439) are observations of the cosmic microwave background (CMB) (see Fig. 22). Observations are virtually indistinguishable from Planck's formula:⁹⁶

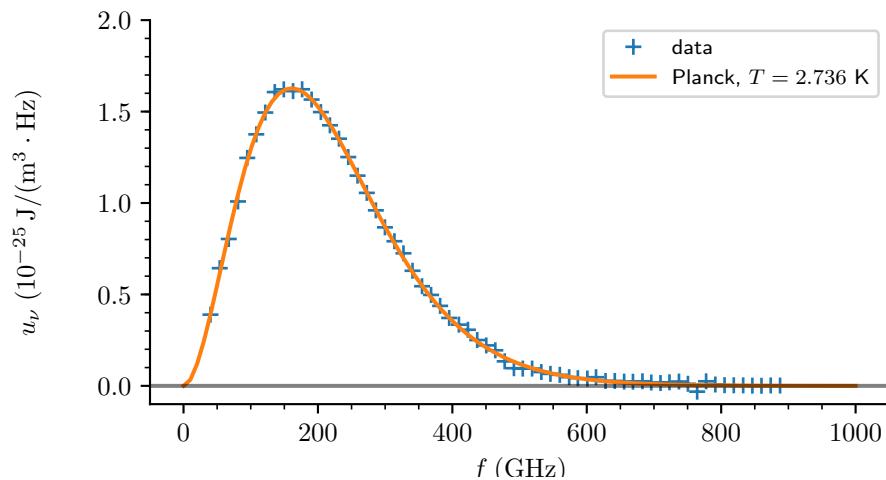


Figure 22: Measurements of the cosmic microwave background (CMB) together with the theoretical Planck distribution (Eq. 439), from H. P. Gush et al., “Rocket measurement of the cosmic-background-radiation mm-wave spectrum”, *Phys. Rev. Lett.* **65**, 537–540 (1990). This distribution is in the microwave regime i.e., $c/(200 \text{ GHz}) \approx 1.5 \text{ mm}$. This $T \approx 3 \text{ K}$ thermal radiation field fills all of space and is of interest to cosmologists. I have chosen this rocket-based data over the much more precise satellite measurements (e.g., Fig. 7.20 of SITP), because of its interesting history A. Grant, “The experiment that confirmed—and almost beat—COBE”, *Physics Today*, [10.1063/PT.6.4.20180830a](https://doi.org/10.1063/PT.6.4.20180830a) (2018).

⁹⁶Roger Penrose remarks:

It is often asserted that the CMB provides the best agreement between an observed phenomenon and the Planck spectrum. However, this is misleading, because COBE merely compares the CMB spectrum with an artificially produced thermal one, so the actual CMB spectrum is only established to be as Planckian as that artificial one.

R. Penrose, *Fashion, faith, and fantasy in the new physics of the universe* (Princeton University Press, Princeton, New Jersey, 2016)

- because electricity and magnetism is neither a pre- nor co-requisite for Phys 358, we “imported” some results without justification (those with the “EM theory” label). Fortunately we are finished doing this — it is against the general spirit of physics. Just to be clear, the blemishes are:

- the radiation pressure due to the “photon gas” given by Eq. 409,
- Wien’s *general* constraint on the functional form of $u_\nu(\nu, T)$ given by Eq. 426, and
- the relationship between cavity spectral energy density $u_\nu(\nu, T)$ and the average energy of each oscillator in Planck’s model, given by Eq. 433.

I think that the best justification of all of these results are contained in Born’s *Atomic Physics*.⁹⁷ You should be able to understand some of these results from material in Phys 342, and all once you take Phys 442.

29 The emission of thermal radiation (SITP pg.’s 300-303)

- Planck developed his theory to explain experimental observations of radiation escaping from a hole cut in cavity (i.e. Fig.’s 20 and 21). We will now look at these types of observations in a bit more detail as — perhaps surprisingly — the thermal radiation that is emitted from the surface of *any* body has a well-defined relationship to the radiation emerging from a cavity and in many cases is quite similar. This universality is what attracted Planck to the problem.
- the system to be studied is:

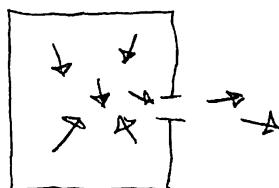


Figure 23: Cavity radiation emerging from a hole. We assume that the radiation in the cavity is replenished quickly enough by the walls of the cavity, so that the radiation in the cavity can be considered to be at the same temperature as the walls and described by Planck’s distribution (Eq. 439.)

- recall that I avoided usage of the “photon” terminology until the very end of the discussion of Planck’s distribution. For computing the emission from the hole I will follow the straightforward approach of Schroeder (pg.’s 300-303) and make use of the photon concept (a classical argument will give the same result, but is a bit less physically intuitive.)
- imagine a thin hemispherical shell of radius R centred on the hole:

⁹⁷M. Born, *Atomic physics*, Reprint of 1969 edition (Dover Publications, New York, 1989), available at <https://archive.org/details/atomicphysics00born>

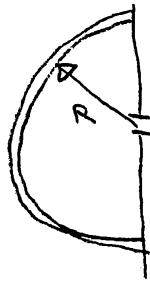


Figure 24: A thin hemispherical shell centred on the cavity hole. *Some* of the photons in the shell will arrive at the hole after $t = R/c$.

- at a time $t = R/c$ later, *some* of the photons in this shell have reached the hole and thus escape. However, the cavity radiation is isotropic, so most of the photons in the shell do not reach the hole at $t = R/c$ since they were not initially travelling towards it.
- to determine what fraction of the photons in the shell *do* reach the hole, we must first determine what solid angle $d\Omega$ that the hole subtends for each point within the shell. Since the cavity radiation is isotropic, comparing this solid angle to the full 4π will tell us the fraction of photons from that part of the shell that *do* make it to the hole and thus escape. For determining the subtended solid angle $d\Omega$ consider:⁹⁸

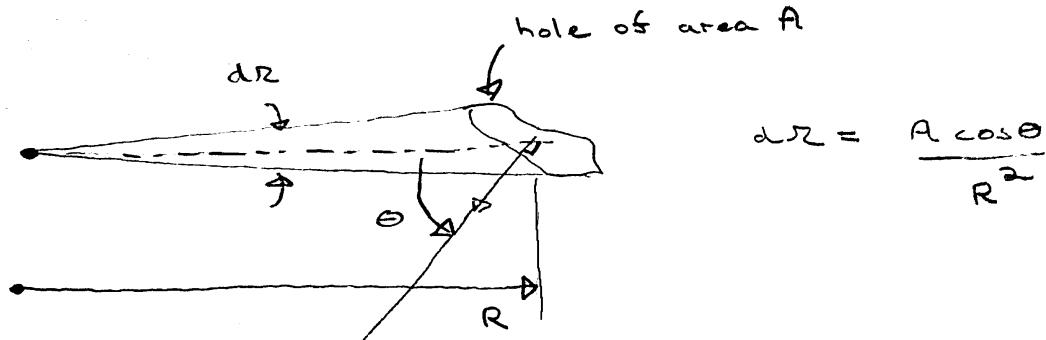


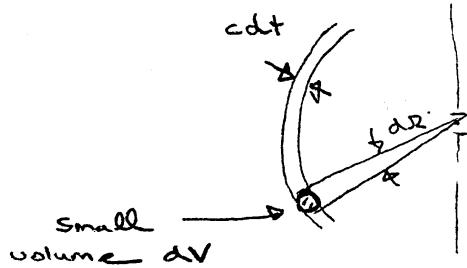
Figure 25: The geometry of determining the solid angle subtended by the hole at different locations (dictated by θ) in the shell.

- so the fraction of photons that escape depends on the location within the shell (through $\cos \theta$):

$$\frac{A \cos \theta}{4\pi R^2}. \quad (442)$$

- we will consider how many photons escape over a small time interval dt , so that it now makes sense to consider a thickness of the hemispherical shell, cdt :

⁹⁸We follow the [normal physics convention](#) and use θ (rather than ϕ) as the polar angle. Sorry mathies.



- the energy that escapes in this small interval of time is (per unit frequency):

$$dE_\nu = \underbrace{dV u_\nu}_{\text{energy in small shell volume per unit frequency}} \times \underbrace{\frac{A \cos \theta}{4\pi R^2}}_{\text{fraction of photons that escape cavity}} \quad (443)$$

- we may write the infinitesimal volume as:

$$dV = cdt R^2 d\Omega \quad (444)$$

$$= cdt R^2 d\theta d\phi \sin \theta \quad (445)$$

and combine with Eq. 443 and integrate over the whole shell:

$$dE_\nu = \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \sin \theta cdt R^2 u_\nu \frac{A \cos \theta}{4\pi R^2} \quad (446)$$

$$= 2\pi cdt u_\nu \frac{A}{4\pi} \int_0^{\pi/2} d\theta \cos \theta \sin \theta \quad (447)$$

$$= cdt u_\nu A \frac{1}{2} \frac{1}{2} \quad (448)$$

so that finally we may write the power emitted per unit frequency, per unit area as

$$\boxed{\frac{dP_\nu}{dA} = \frac{c}{4} u_\nu} \quad (449)$$

and integrating over u_ν (as per Eq. 441), gives the **Stefan-Boltzmann law**:

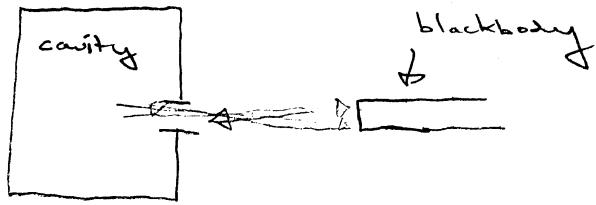
$$\boxed{\frac{dP}{dA} = \sigma T^4}, \quad (450)$$

where the **Stefan-Boltzmann constant**

$$\sigma := \frac{2\pi^5 k^4}{15 h^3 c^2}, \quad (451)$$

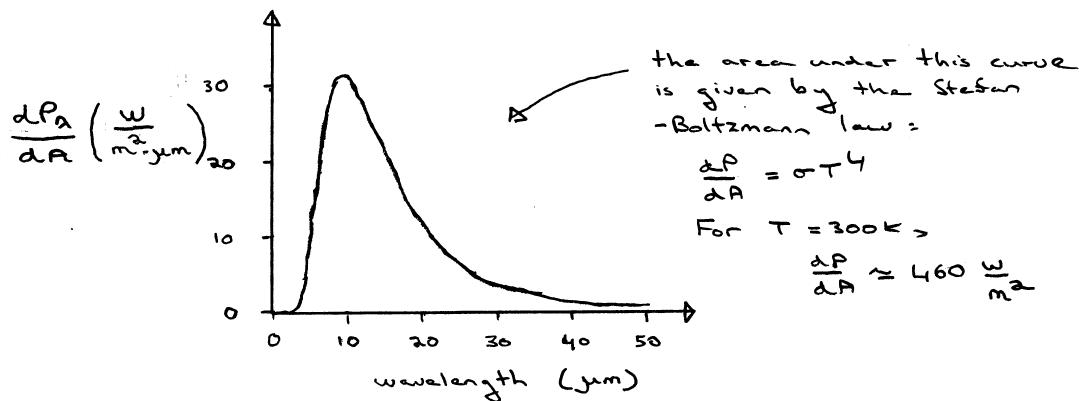
which evaluates to: $\sigma = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}$.

- let us imagine a body that absorbs all incident radiation — a **blackbody** — placed to catch radiation emerging from a cavity:



If the cavity radiation and the blackbody radiation are at the same temperature, then a blackbody *must* emit radiation with the same properties as the cavity radiation. Otherwise there would be net flow of energy between the cavity and blackbody, and they would not be at thermal equilibrium, despite being at the same temperature. Thus the cavity radiation that we have been studying is in fact *blackbody radiation*, and we shall now call it so.

- shown below is the power emitted per unit area *per unit wavelength* of a blackbody at room temperature (300 K):



We see that thermal emission from blackbodies occurs in the infrared. Not only that, a small change in temperature gives a large change in emission:

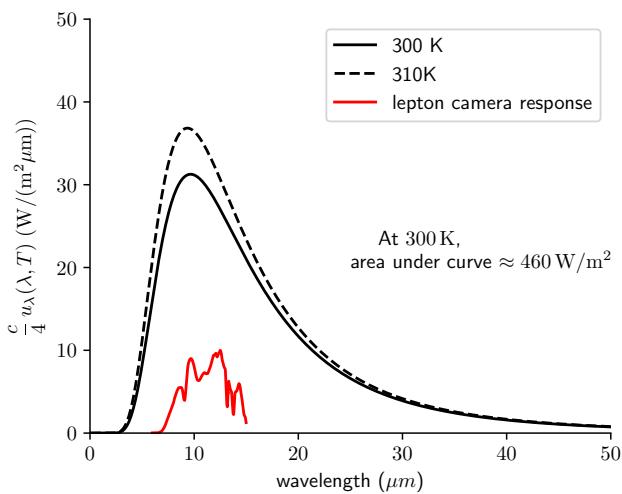


Figure 26: At room temperature, blackbody emission is in the infrared and highly sensitive to temperature. Cameras (such as Lepton shown here) may be designed with high sensitivity in this infrared range.

- surprisingly, liquid water acts like a blackbody at room temperature, so that an infrared camera gives some interesting images:



Figure 27: Two cups of water, one at 21 °C, the other at 34 °C, viewed in visible and in infrared (7–15 μm), taken with a FLIR ONE camera. Source: JDDM

- most objects that look white (or even transparent, like water) to us at visible wavelengths absorb strongly in the infrared, and thus are strong blackbody radiators. A good example is snow.
- we characterize deviations from pure blackbody emission using the **emissivity** $\epsilon(\nu)$, such that:

$$\frac{dP_\nu}{dA} = \epsilon(\nu) \frac{c}{4} u_\nu. \quad (452)$$

In this manner, a blackbody is defined to be an object with $\epsilon(\nu) = 1$.

- here are some emissivities of interest:

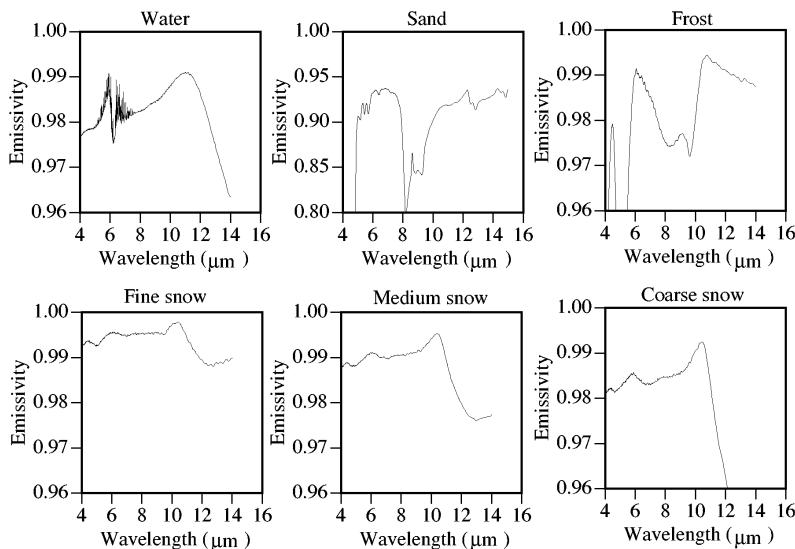


Figure 28: The emissivity of many materials is near one in the infrared. Source: Wilber et al., *Surface emissivity maps for use in satellite retrievals of longwave radiation*, NASA/TP-1999-209362

- often $\epsilon(\nu)$ is sufficiently constant over a range of frequencies that it may be approximated as constant, so that

$$\frac{dP}{dA} \approx \epsilon\sigma T^4. \quad (453)$$

For example, this formula works well for snow, with $\epsilon \approx 0.98$ for the temperatures that we normally find snow. Again, this is somewhat surprising, as snow certainly doesn't look black in the visible!

- we haven't said all that we can about thermal emission, but enough so that we can discuss our next subject intelligently.

30 The sun

- to a reasonable degree of accuracy, the sun emits like a blackbody at 6000 K.^{99,100}

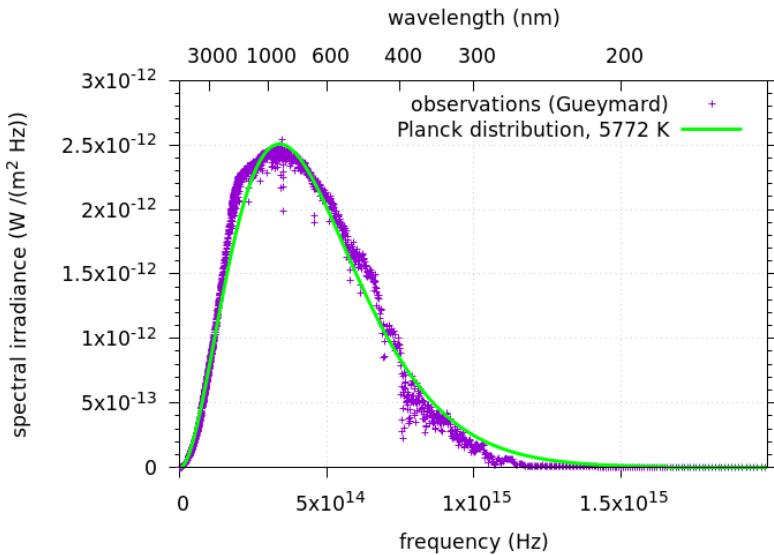


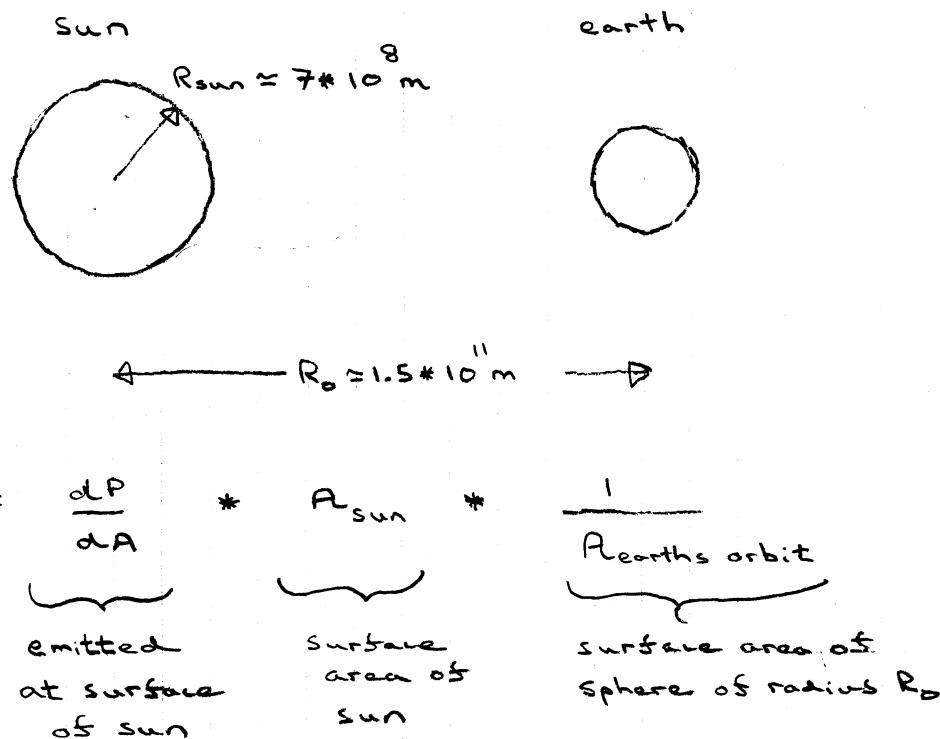
Figure 29: The sun emits like a blackbody. The “Planck distribution” is computed using Eq. 449. The data is from C. A. Gueymard, “The sun’s total and spectral irradiance for solar energy applications and solar radiation models”, *Solar Energy* **76**, 423–453 (2004) (downloadable at: <https://www.nrel.gov/grid/solar-resource/assets/data/newguey2003.txt>)

- given the assumption that the sun emits like a blackbody, what is the solar radiation (power / unit area) at the top of the earth’s atmosphere (before any scattering or absorption)? This quantity is known as the **solar constant** ($= S_0$).

⁹⁹That the sun is *not* a “perfect” blackbody has been the source of many interesting discoveries, including:

(1) the spectral lines of helium, observed before helium was found on earth!
(2) continuum absorption due to photodetachment: $H^- + h\nu \longrightarrow H + e^-$, leading to the understanding that H^- is stable (again before its observation on earth).

¹⁰⁰Do not forget, as per Problem 1.55 of SITP, that the centre of the sun is much hotter ($\approx 10^7$ K). But it is the sun’s *surface* temperature that is relevant here, since photons emitted near the centre are absorbed before they can make their way to the surface.



Simplifying gives:

$$S_0 = \frac{dP}{dA} \left(\frac{R_{\text{sun}}}{R_o} \right)^2 \quad (454)$$

and using the Stefan-Boltzmann law (Eq. 450):

$$S_0 = \sigma T^4 \left(\frac{R_{\text{sun}}}{R_o} \right)^2 \quad (455)$$

and substituting the relevant quantities gives:

$$S_0 \approx 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4} \times (5770 \text{ K})^4 \times \left(\frac{7 \times 10^8 \text{ m}}{1.5 \times 10^{11} \text{ m}} \right)^2 \quad (456)$$

$$S_0 \approx 1370 \frac{\text{W}}{\text{m}^2}$$

(457)

- this value of S_0 varies slightly with sunspot activity and the earth's distance to the sun (solar "constant" is a bit of a misnomer).

31 The temperature of the earth

- we will now estimate the temperature of the earth using some models, which although incredibly simple, give a good deal of insight.
- roughly 30% of sunlight incident on the earth is scattered into space (mostly by clouds; aerosols make a smaller contribution); this quantity is known as the **albedo**.

- thus the total solar power absorbed by the earth is:

$$P \approx S_0(1 - \text{albedo})\pi R_e^2. \quad (458)$$

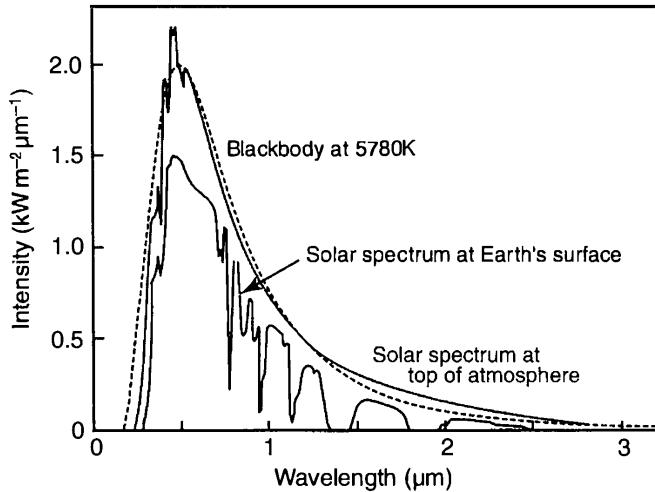


Figure 30: A large fraction of the sun’s radiation at top of our atmosphere gets to the earth’s surface. Source: Fig. 2.3 of F. W. Taylor, *Elementary climate physics* (Oxford University Press, New York, 2005)

- to stay at a constant temperature, the earth needs to radiate away the same power into outer space (there is no other way to get rid of energy).¹⁰¹
- recall from Fig. 28 that the emissivities of many materials near one in infrared. Thus we expect that the earth’s surface will emit like a blackbody in the infrared, with a total power:

$$P = \sigma T_e^4 4\pi R_e^2. \quad (459)$$

- equating Eq.’s 459 and 458 for a steady-state T_e gives:

$$S_0(1 - \text{albedo})\pi R_e^2 = \sigma T_e^4 4\pi R_e^2. \quad (460)$$

Rearranging gives:

$$T_e = \left(\frac{S_0(1 - \text{albedo})}{4\sigma} \right)^{1/4}. \quad (461)$$

Substituting the relevant numbers:

$$T_e \approx \left(\frac{1370 \frac{\text{W}}{\text{m}^2} (1 - 0.3)}{45.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}} \right)^{1/4} \quad (462)$$

$$\approx 255 \text{ K } (-17^\circ\text{C}) \quad (463)$$

That’s a bit cold, but not too far off from the “average” temperature of the earth $\approx 14^\circ\text{C}$, when one considers the *absolute* temperatures; the relative error being $\approx 10\%$.

¹⁰¹The heat flux towards the earth’s surface from its interior $\approx 0.1 \text{ W/m}^2$ is rather small in comparison to the solar contribution (see [wikipedia](#)).

- our calculation assumed that the radiation emitted by the earth's surface travels directly into outer space. This assumption is not true — atmospheric CO₂, H₂O, and O₃ (ozone) absorb significant amounts of infrared:

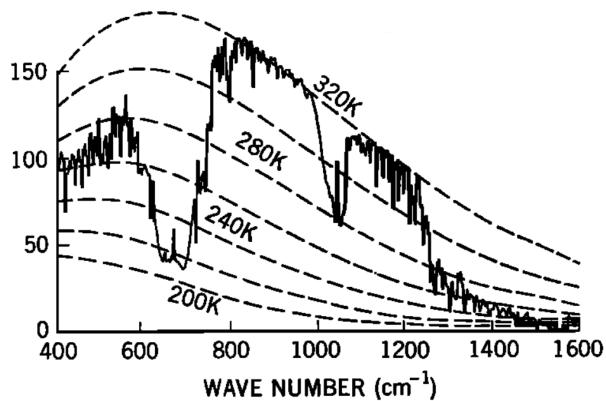
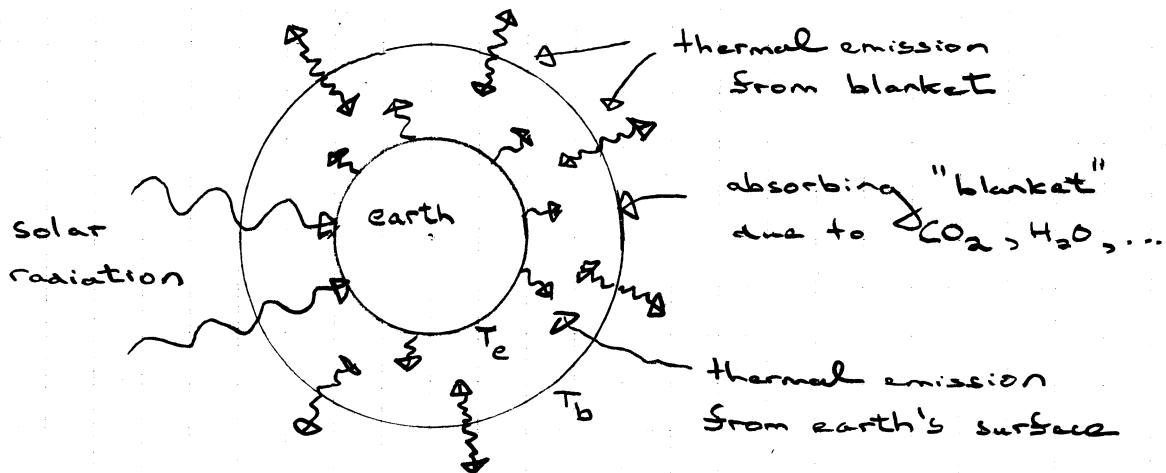


Figure 31: To the left is a spectrum recorded looking down at earth (North Africa) from a satellite ($10\ \mu\text{m}$ is equivalent to $1000\ \text{cm}^{-1}$). The dotted lines are the theoretical blackbody emission curves for different temperatures — the reduced emission at certain wavelengths indicates absorption of the outgoing surface thermal emission by the atmosphere. Source: Figure 11 of R. A. Hanel et al., "The Nimbus 4 infrared spectroscopy experiment: 1. Calibrated thermal emission spectra", *Journal of Geophysical Research* **77**, 2629–2641 (1972)

- we can account for the absorption of infrared by CO₂ in the atmosphere with a simple model, in which the atmosphere acts like a “zero thickness” blanket of temperature T_b :



(the radius of the blanket in comparison to the earth's radius is exaggerated in this diagram — it is actually only about the atmosphere scale height $\approx 8\ \text{km}$ above the earth's surface).

- the blanket radiates *both* outwards (to space) and inwards (to earth). For an earth surface temperature constant in time:

$$P_0 + A\sigma T_b^4 = A\sigma T_e^4. \quad (464)$$

Considering that the blanket radiates *both* outwards (to space) and inwards (to earth), and absorbs the outgoing radiation from the earth's surface, to obtain a blanket temperature T_b constant in time:

$$A\sigma T_e^4 = 2A\sigma T_b^4. \quad (465)$$

Combining Eq.'s 465 and 464 gives:

$$P_0 = A\sigma T_b^4, \quad (466)$$

and thus by Eq. 463, $T_b \approx 255\text{ K}$. Rearranging Eq. 465 gives:

$$T_e = 2^{1/4} T_b \quad (467)$$

$$\approx 2^{1/4} 255\text{ K} \quad (468)$$

$$\approx 303\text{ K} \quad (30^\circ\text{C}) \quad (469)$$

which is certainly higher than the earth's surface temperature (with a relative error of $\approx 6\%$).

- summarizing the results of our two simple models:

1. with no absorption due to the atmosphere:

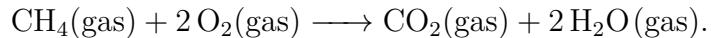
$$T_e \approx -17^\circ\text{C}$$

2. with a completely absorbing “blanket-like” atmosphere:

$$T_e \approx 30^\circ\text{C}.$$

as compared with the actual average earth temperature of 14°C .

- as Fig. 31 illustrated, our atmosphere is not *completely* absorbing in the infrared. Some thermal radiation from the surface of the earth passes through the blanket. Thus, that the earth's actual temperature is in between our two simplistic estimates makes sense.
- earlier in the course (e.g., SITP Problem 1.50), you examined the heat released in the combustion reaction:



All hydrocarbon combustion reactions (burning gasoline, coal, wood, natural gas, etc...) produce CO_2 .

- in ≈ 1769 James Watt patented an improved steam engine design, which saw widespread adoption: the *first* heat engine in widespread usage. Since then, the CO_2 in the atmosphere has dramatically increased:

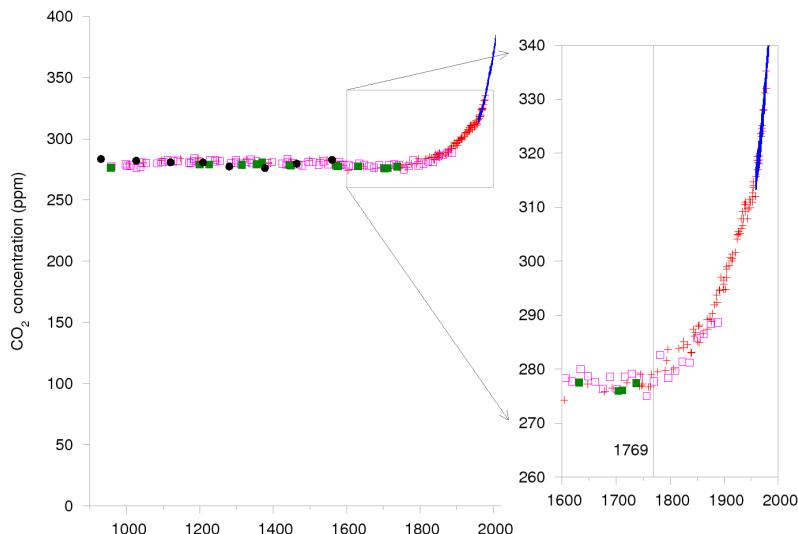


Figure 32: Source: Figure 1.4 of D. MacKay's *Sustainable energy without all the hot air* <https://www.withouthotair.com>

- this increase in CO₂ brings us closer to the full “blanket” scenario.
- it is *total* amount of CO₂ in the atmosphere that matters: i.e., the integral of the rate of emission. Unfortunately, the CO₂ emission *rate* is currently increasing:

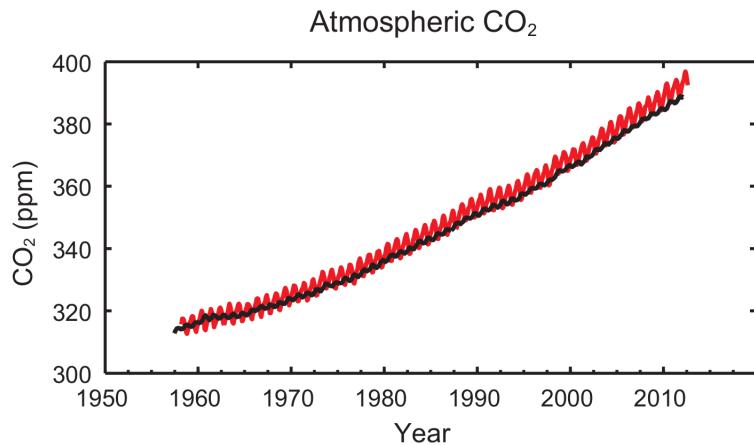


Figure 33: Note the oscillation with a period of a year. Photosynthesis takes CO₂ and H₂O to produce carbohydrates for energy, and then “burning” releases CO₂. A yearly periodicity in the CO₂ then arises because there is more land mass in the Northern hemisphere. Source: Figure SPM.4 (pg 12) of IPCC, Climate Change 2013: The Physical Science Basis, <https://www.ipcc.ch/report/ar5/wg1/>

- so what will happen in the future? It depends on us:

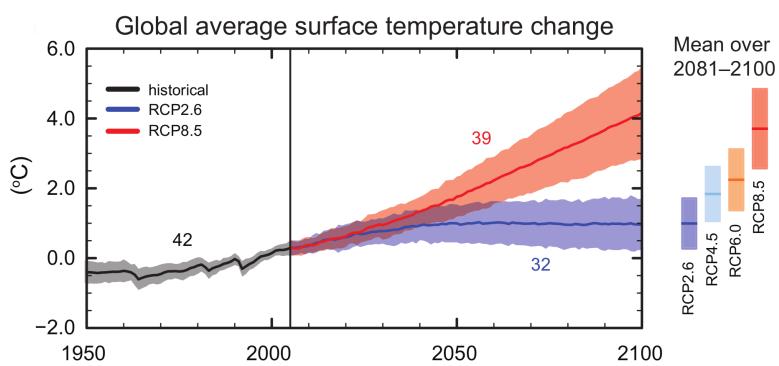


Figure 34: The different simulated scenarios are labelled using the **Representative Concentration Pathways** (RCPs) terminology, corresponding to different possible future emissions of greenhouse gases. “Business as usual” (our current trajectory (?)), is somewhere between RCP6.0 and RCP8.5, but deciding where is somewhat contentious. An all-out effort to reduce emissions (unlikely at this point) is RCP2.6. Source: Figure SPM.7 (pg 21) IPCC, Climate Change 2013: The Physical Science Basis, <https://www.ipcc.ch/report/ar5/wg1/>

- going beyond the simple models is a challenging. The quantitative, critical skills that you have developed as physics students are useful.¹⁰² As announced in *Nature*:

Physicists, your planet needs you.

- and non-specialists are important as well. How may quantitative scientific ideas be communicated to the general public? Here are two wonderful examples:
<https://xkcd.com/1732/> and <https://youtu.be/0WXoRSIxIu>

¹⁰²It is surprising how many topics from earlier in this course are relevant to climate change: the Einstein model, the adiabatic lapse rate, combustion, heat engines, batteries/fuel cells (in relation to alternate energy sources).

Part V

Appendices

A Mathematical prerequisites

Although basic multi-variable calculus is a pre-requisite for these notes, some of the results that are important here tend to be slightly overshadowed by more lofty results in mathematics courses. More specifically, we will make use of:

1. the “triple-product rule”. See “Snowy mountain friend” and “Breaking rails” in the [extended example problems](#) and SITP Problem 1.46 (highly recommended).
2. “derivatives under a change of coordinates”. See “Kitchener coordinates” in the [extended example problems](#).

After working through these examples, you should be able to argue why we use a “special notation” for derivatives in thermodynamics — specifically a notation that indicates which variables are to be held constant as the derivative is being taken (i.e., the subscript to the brackets, such as V in $(\partial U / \partial T)_V$).

B Galilean thermometers and buoyancy

The troubled undergraduate’s primary difficulty lay in conceiving how anything could float. This was so completely removed by Dr Routh’s lucid explanation that they went away sorely perplexed as to how anything could sink!

From the obituary of Routh, quoted at [MacTutor](#).

- recall from Section 4.1 that liquid-in-glass thermometers rely on a fixed amount of liquid changing its density with temperature, so that the volume occupied by the liquid changes, and the liquid-vapour boundary moves.
- another thermometer that relies on the change in liquid density with temperature is the **Galilean thermometer**:

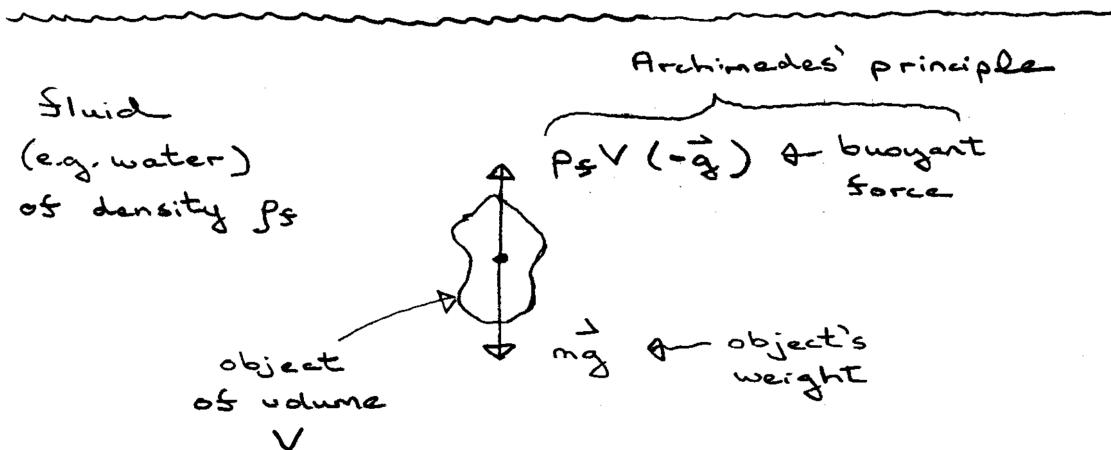


Figure 35: A Galilean thermometer. Each “floater” (attractively coloured here) is labelled with a temperature. The temperature of the fluid is bounded from above by the lowest temperature label on the floaters at the top, and bounded from below by the highest temperature label on the floaters that have sunk. If a hair dryer is used to heat the thermometer (which I normally do in the lectures), all of the “floaters” sink to the bottom (e.g., <https://youtu.be/wRVEI9hpc9A?t=138>; note the indicated temperature on the adjacent liquid-in-glass thermometer). Clearly to understand how this all works, we need to know why objects sink or float in a fluid, namely **buoyancy**.
Source: JDDM.

- since buoyancy will show up several times in this course — particularly in applications — we will take a brief detour to discuss it. (As probably apparent, the Galilean thermometer is not particularly precise; but it is an instructive visualization of buoyancy.)
- the essence of buoyancy is **Archimedes' principle**:

Any object, totally or partially immersed in a fluid or liquid, is buoyed up by a force equal to the weight of the fluid displaced by the object (as given by [wikipedia](#)).

- before we explain *why* the principle holds, we will first familiarize ourselves with *what* it says, in the context of the Galilean thermometer.
- consider the net force on an object submerged in a fluid:



- the net force on the object is a combination of the upwards buoyant force and the downwards force of gravity:

$$\text{net force} = \rho_f V(-\vec{g}) + m\vec{g}. \quad (470)$$

Taking the projection along $-\vec{g}$ i.e., upwards:

$$\text{net upwards force} = \rho_f V g - mg \quad (471)$$

Suppose that the object has a uniform mass density ρ_o . Then $m = \rho_o V$, and thus

$$\text{net upwards force} = V g (\rho_f - \rho_o), \quad (472)$$

making it clear that if:

- $\rho_f > \rho_o \Rightarrow$ the object will float (e.g., wood in water), and if
- $\rho_f < \rho_o \Rightarrow$ the object will sink (e.g., lead in water).
- if a body does not have a uniform mass density, we may compute:

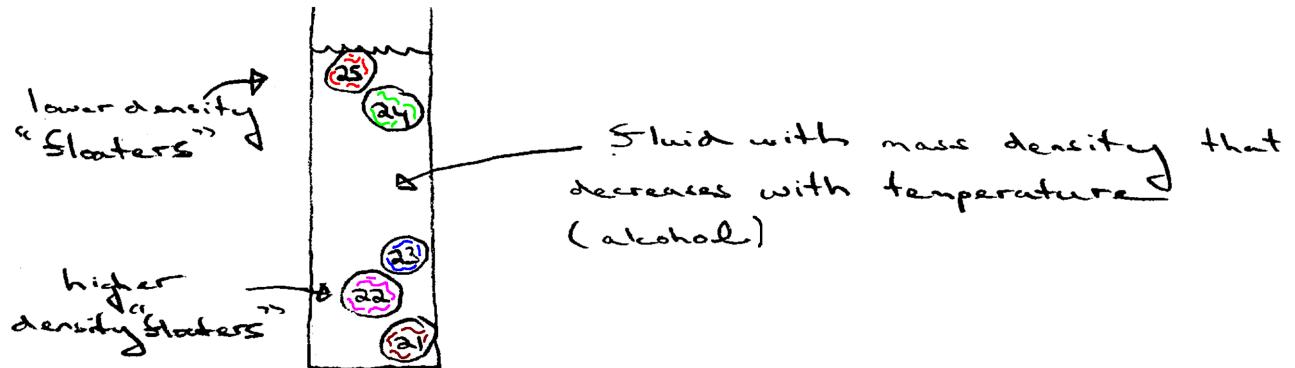
$$\text{net upwards force} = V g (\rho_f - \bar{\rho}_o) \quad (473)$$

where $\bar{\rho}_o$ is the *average* mass density of the object:

$$\bar{\rho}_o := \frac{m_o}{V} \quad (474)$$

and compare $\bar{\rho}_o$ to ρ_f to determine if the body will sink or float.

- Archimedes' principle explains the operation of the Galilean thermometer; the density of the surrounding fluid varies with temperature:



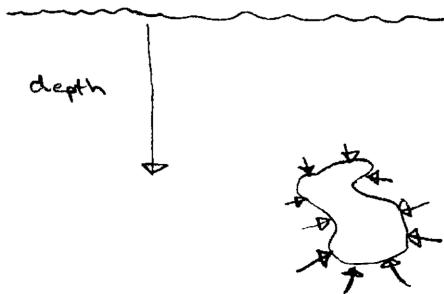
- how do we determine the temperature from a Galilean thermometer?
- the temperature of the fluid is in between the values indicated by the lowest temperature "floater" that is floating and highest temperature "floater" that has sunk. In the case illustrated above, the temperature is between 23 °C and 24 °C.
- how should we construct and label each floater? We need to know the fluid density as a function of temperature T , i.e., $\rho_f(T)$. If the i th floater is to correspond to temperature T_i , then its average density $\bar{\rho}_i$ must satisfy¹⁰³

$$\bar{\rho}_i = \rho_f(T_i). \quad (475)$$

¹⁰³We are simplifying by assuming that the density of each floater is independent of temperature.

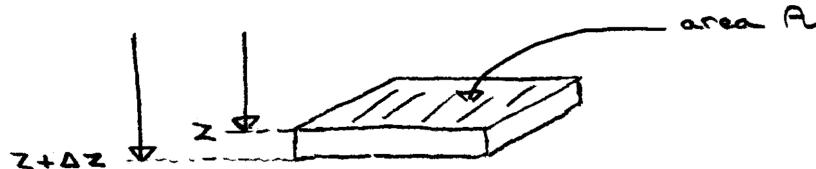
Then, by Archimedes' principle this i th floater will have **neutral** buoyancy when the fluid has temperature T_i . Continuously adjusting the density of homogeneous floaters would be difficult; so instead all floaters are of identical size and density (lower than that of fluid), but metal tags of varying size are added to each, of density higher than fluid, in such a way as to obtain each desired average density $\bar{\rho}_i$ for the combined floater and tag.

- now let us explain Archimedes' principle from more fundamental laws.
- the buoyant force is due to the pressure of the surrounding fluid on the object:



Pressure is an **isotropic** property of a fluid in mechanical equilibrium (**Pascal's principle**). The fluid pressure increases with depth.

- the surrounding fluid pushes the object upwards more than downwards. Why?
- as depth increases, the pressure of the fluid increases (a phenomena that scuba divers are familiar with). By how much? Consider a thin slab of the fluid:



with the convention that increasing depth corresponds to increasing z . The slab is in mechanical equilibrium — there must be zero net force acting on the slab.

The fluid pressure exerts a force on the top face:

$$F_{\text{top},z} = P(z)A \quad (476)$$

and on the bottom face:

$$F_{\text{bottom},z} = -P(z + \Delta z)A. \quad (477)$$

The force of gravity also acts downwards on the slab

$$F_{g,z} = \underbrace{A \Delta z \rho_f g}_m \quad (478)$$

and thus for mechanical equilibrium:

$$0 = P(z)A - P(z + \Delta z)A + \rho_f g A \Delta z. \quad (479)$$

Rearranging gives:

$$\frac{P(z + \Delta z) - P(z)}{\Delta z} = \rho_f g. \quad (480)$$

Taking the limit $\Delta z \rightarrow 0$, gives a simple (the simplest?) differential equation:

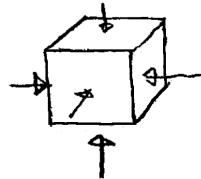
$$\frac{dP(z)}{dz} = \rho_f g, \quad (481)$$

which has the solution:

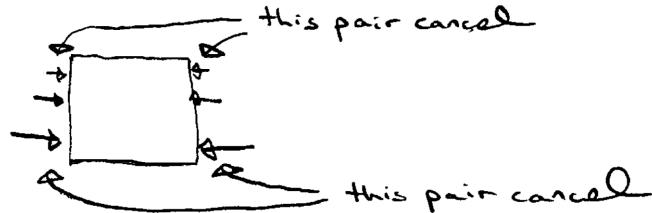
$$P(z) = \rho_f g z + P_0 \quad (482)$$

where P_0 is the pressure within the fluid at $z = 0$; e.g., at a water surface it is the atmospheric pressure ($P_0 \approx 1$ bar).¹⁰⁴

- before showing that this variation of pressure with depth implies Archimedes' principle for an arbitrarily shaped object, let's look at a cube first:



- the net force due to the pressure on the four sides will vanish, as all the forces come in equal and opposite pairs:



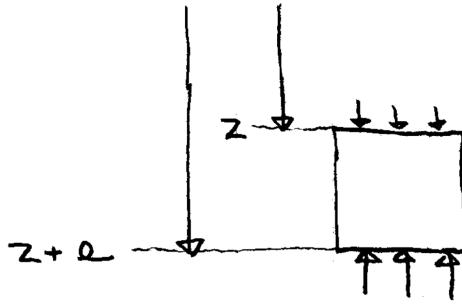
- however, the force due to the pressure on the bottom of the cube *will not* cancel the force due to the pressure on the top of the cube, because the pressure of the surrounding fluid is larger at the bottom compared to the top of the cube. With an $\ell \times \ell \times \ell$ cube:

¹⁰⁴Problem 1.16 of SITP asks for the pressure variation with altitude in the earth's atmosphere. The relevant differential equation is similar to Eq. 481 — with the same justification — except complicated by the pressure dependence of the density:

$$\frac{dP}{dz} = -\rho_{\text{air}}(P)g,$$

where the negative sign appears because z refers to altitude (not depth). Assuming constant temperature, composition, and the ideal gas law:

$$\rho_{\text{air}}(P) = \frac{P}{RT} \left\langle \frac{m}{n} \right\rangle_{\text{air}}.$$



we may use the pressure variation with depth given by Eq. 482 to obtain:

$$\text{net buoyant force downwards} = \overbrace{\ell^2[\rho_f g z + P_0]}^{\text{top face}} - \overbrace{\ell^2[\rho_f g(z + \ell) + P_0]}^{\text{bottom face}} \quad (483)$$

$$= \ell^2 \rho_f g [z - (z + \ell)] \quad (484)$$

$$= -\ell^3 \rho_f g \quad (485)$$

$$= -V \rho_f g, \quad (486)$$

in agreement with Archimedes' principle (the negative sign indicating that the force is upwards).

- now what about an arbitrarily shaped body? For this we will use vector calculus — more specifically the **divergence theorem**. Some of you will have studied vector calculus in the pre-requisite math classes;¹⁰⁵ some will not. Whether you have or not, I recommend that you study the following derivation (as an application of vector calculus), although it is not testable material per se. However, you *are* required to know the result, namely Archimedes' principle for arbitrarily shaped objects.
- the net force due to the pressure of the surrounding fluid is:

$$\vec{F} = \oint_{\text{surface of body}} P(z)(-\hat{n})da. \quad (487)$$

In what follows let's use the convention from Griffiths' *Introduction to electrodynamics*: $d\vec{a} := \hat{n}da$.)

What is the z (vertical) component of the force? Dot both sides with \hat{z} , and define $F_z := \hat{z} \cdot \vec{F}$.

$$F_z = -\hat{z} \cdot \oint P(z)d\vec{a} \quad (488)$$

$$= -\oint P(z)\hat{z} \cdot d\vec{a} \quad (489)$$

Remember the divergence theorem! (a purely mathematical result). For all non-pathological

¹⁰⁵At the University of Waterloo, students in the Physics program will have studied vector calculus; whereas some Mathematical Physics students will not (yet).

vector fields \vec{A} :

$$\oint_{\text{closed surface}} \vec{A} \cdot d\vec{a} = \int_{\text{enclosed volume}} dV \nabla \cdot \vec{A} \quad \text{the divergence of } \vec{A} \quad (490)$$

For the comfort of familiarity, recall that in electromagnetism, the divergence theorem, together with Maxwell's first equation gives us:

$$\oint \vec{E} \cdot d\vec{a} = \int dV \nabla \cdot \vec{E}; \quad (491)$$

inserting the *physics* of Maxwell's first law:

$$= \int dV \frac{\rho}{\epsilon_0} \quad (492)$$

$$= \frac{Q_{\text{enclosed}}}{\epsilon_0}, \quad (493)$$

a result that should be familiar if you've studied electricity and magnetism (the integral form of Gauss' law).

For our problem, the vector field is $\vec{A} = -P(z)\hat{z}$, so that applying the divergence theorem (Eq. 490) to:

$$F_z = - \oint P(z)\hat{z} \cdot d\vec{a} \quad (494)$$

gives:

$$= - \int dV \nabla \cdot (P(z)\hat{z}). \quad (495)$$

What is $\nabla \cdot (P(z)\hat{z})$? Using Eq. 482:

$$\nabla \cdot (P(z)\hat{z}) = \frac{\partial}{\partial z} P(z) \quad (496)$$

$$= \frac{\partial}{\partial z} (\rho_f g z + P_0) \quad (497)$$

$$= \rho_f g. \quad (498)$$

Thus, by Eq. 495:

$$F_z = - \int dV \rho_f g \quad (499)$$

$$= -\rho_f g \int dV \quad (500)$$

$$= -V \rho_f g. \quad (501)$$

The mass of the displaced fluid is $V \rho_f$ and the force is negative because our convention was that z increases with increasing depth. Summarizing in words:

the buoyant force upwards is equal to the weight of the displaced fluid.
i.e., Archimedes' principle for an arbitrarily object \square .

- note that since $\vec{\nabla} \cdot (P(z)\hat{x}) = 0$ and $\vec{\nabla} \cdot (P(z)\hat{y}) = 0$, the divergence theorem tells us that $F_x = 0$ and $F_y = 0$. i.e., the pressure of the fluid does not cause any “sideways” force.
- you are driving along in your car and you suddenly slam on your brakes. Your double whopper flies out of your hands onto the dash. What happens to the helium balloon¹⁰⁶ in your car?

C Comments on the equipartition theorem

- in Section 5 we looked at heat capacities of various gas phase molecules as a function of temperature (Fig. 5).
- we briefly mentioned that the observed C_V/N 's, and the seemingly special values of $\frac{3}{2}k$, $\frac{5}{2}k$, $3k$ (all integer multiples of $\frac{1}{2}k$) could be partially rationalized using the **equipartition theorem**, which gives the internal energy of a gas of N molecules as:

$$U = f \frac{1}{2} N k T \quad (502)$$

where f is the number of **degrees of freedom** per molecule that contribute quadratic-like terms to the energy:

- $f = 3$ for atoms and molecules that are moving, but have no other internal motions, since $U/N = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$. Setting $f = 3$ in Eq. 502 gives Eq. 26, corresponding to the noble gases (He, Ne, Ar, Kr, Xe) of Fig. 5. At higher temperatures than Fig. 5 even the noble gases will exhibit $f \neq 3$ due to thermal excitation of their electrons.¹⁰⁷
- $f = 5$ for a diatomic molecule that is both moving and rotating. That there are two additional quadratic degrees of freedom and not three due to rotation of a diatomic is not obvious — it is a consequence of quantum mechanics.¹⁰⁸
- $f = 7$ for a diatomic molecule that is moving, rotating and vibrating. The two additional quadratic-like degrees of freedom arise from the relative motion of the two atoms, for which there will be a corresponding kinetic energy term and a spring-like quadratic energy term.

¹⁰⁶Buoyancy explains the operation of various types of balloons. An interesting discussion of the connection between ballooning and the development of science is given in <http://doi.org/dcppks>, and an entertaining history of ballooning is:

<https://archive.org/details/TheMontgolfierBrothersAndTheHotAirBalloon>

(Although some of the scientific explanations in this video leave a bit to be desired.)

¹⁰⁷Monatomic gases of non-noble elements are difficult to observe — the atoms tend to combine to form molecules e.g. two oxygen atoms form a diatomic oxygen molecule. At higher temperatures, where monatomic non-noble gases can be more readily observed, thermal excitation of their internal energy levels are usually significant, complicating matters. (However, later I will use monatomic Hg gas as an example of some issues related to entropy in Part II of these notes.)

¹⁰⁸For more details (beyond the scope of this course), see: C. A. Gearhart, “Specific heats and the equipartition law in introductory textbooks”, *Am. J. Phys.* **64**, 995–1000 (1998)

- the equipartition “theorem” is a purely classical result and as the experimentally determined C_V 's of Fig. 5 show, is not generally true — the equipartition theorem predicts temperature independent C_V 's. Instead, Eq. 502 with integer f 's is *sometimes* a good approximation over a limited temperature range. For example, we see that at room temperature $C_V \approx \frac{5}{2}NkT$ for N₂ and O₂. These molecules are moving and rotating, but not vibrating at room temperature. On the other hand, F₂ has a higher C_V at room temperature, since roughly speaking, F₂ exhibits more vibrational excitation at room temperature compared to O₂ and N₂.
- although SITP Section 1.3 says more about the equipartition theorem, I am uncomfortable doing so, as we cannot derive it yet. Once you can derive the equipartition theorem,¹⁰⁹ you will better understand when it can be used and why it is not generally true.
- if the preceding discussion has seemed a bit too focused on confusing details, I apologize. Here are my excuses:
 - (1) I disagree with SITP's introduction of the equipartition theorem so early. But since I wish to refer to the book, I need to address this issue somehow. This is partially because:
 - (2) the first time that I taught Phys 358, I observed that without my cautions the equipartition theorem ended up being used incorrectly (on exams(!)).
- in summary: for now (in Phys 358) only apply the equipartition theorem when you are presented with some rationale on why you may do so, or in the two cases where you are certain that it can be used: monatomic ideal gases at temperatures low enough so that internal excitations are not important ($f = 3$) (i.e., the entire temperature range of Fig. 5) and air around room temperature and pressure ($f = 5$).

D Euler's homogeneous function theorem and the virial theorem

D.1 Euler's homogeneous function theorem

- Euler's homogeneous function theorem (EHFT) has several applications, including the virial theorem that we will discuss in the next section.
- let us start by introducing the *type* of functions that EHFT applies to. Consider an expression for the total kinetic energy of a set of particles:

$$T = \frac{1}{2} \sum_i m_i v_i^2. \quad (503)$$

Now let us suppose that we scale all of the velocities by a factor α , so that $v'_i = \alpha v_i$. The

¹⁰⁹The equipartition theorem is derived in SITP, Section 6.3, and in the University of Waterloo course: PHYS 359, *Statistical Mechanics*. The experimentally observed temperature dependent heat capacity of H₂ and other violations of the equipartition theorem contributed to the development of quantum mechanics. In retrospect, the equipartition theorem should have been called the **equipartition approximation**. (I will not object if you call it so.)

kinetic energy with the scaled velocities is:

$$T' = \frac{1}{2} \sum_i m_i v_i'^2 \quad (504)$$

$$= \frac{1}{2} \sum_i m_i (\alpha v_i)^2 \quad (505)$$

$$= \alpha^2 \frac{1}{2} \sum_i m_i v_i^2 \quad (506)$$

$$= \alpha^2 T. \quad (507)$$

- likewise, let us consider the total potential energy of a group of particles with a gravitational interaction:

$$V = \sum_{i \neq j} \frac{G m_i m_j}{|\vec{r}_i - \vec{r}_j|}. \quad (508)$$

If we scale each position “vector” by a positive factor α ($\vec{r}'_i = \alpha \vec{r}_i$), then the new potential energy is

$$V' = \alpha^{-1} V. \quad (509)$$

- these T and V examples illustrate the defining property of **positive homogeneous functions**. Specifically, a function of several variables is considered a “positive homogeneous of degree k ”, if for all $\alpha > 0$:

$$f(\alpha a, \alpha b, \dots) = \alpha^k f(a, b, \dots). \quad (510)$$

e.g., T as given in Eq. 503 is a positive homogeneous function of degree 2, and V as given in Eq. 508 is a positive homogeneous function of degree -1 .

- positive homogeneous functions are of interest to us here because they satisfy **Euler's homogeneous function theorem** (EHFT), which states that if f is a positive homogeneous function of order k , then¹¹⁰

$$a \frac{\partial f(a, b, \dots)}{\partial a} + b \frac{\partial f(a, b, \dots)}{\partial b} + \dots = k f(a, b, \dots). \quad (511)$$

This equality may readily be seen by starting with a positive homogeneous function of order k , for which by definition:

$$f(\alpha a, \alpha b, \dots) = \alpha^k f(a, b, \dots), \quad (512)$$

for all $\alpha > 0$. Differentiating both sides with respect to α :

$$a \frac{\partial f(\alpha a, \alpha b, \dots)}{\partial a} + b \frac{\partial f(\alpha a, \alpha b, \dots)}{\partial b} + \dots = k \alpha^{k-1} f(a, b, \dots). \quad (513)$$

Since this is true for all $\alpha > 0$, we may set $\alpha = 1$, to obtain

$$a \frac{\partial f(a, b, \dots)}{\partial a} + b \frac{\partial f(a, b, \dots)}{\partial b} + \dots = k f(a, b, \dots), \quad (514)$$

as required \square .

¹¹⁰Equivalently, in the notation of vector calculus: $\vec{r} \cdot \vec{\nabla} f(\vec{r}) = k f(\vec{r})$.

- although not directly relevant to what follows, the additional constraints required to ensure that the converse is true — namely that a function that satisfies Eq. 514 is a homogeneous function — may be of interest to the mathematically minded. See pg 120 of E. Barbeau, *Mathematical fallacies, flaws, and flimflam*, Spectrum Series (Mathematical Association of America, Washington, DC, 2000).

D.2 The virial theorem

- the virial theorem¹¹¹ relates the long time average of the potential energy and kinetic energy of a group of particles.
- to derive the virial theorem, we first consider the kinetic energy of a set of point particles. As discussed in the previous section, their kinetic energy is given by a positive homogeneous function of order 2, and thus by EHFT:

$$2T = \sum_i v_i \frac{\partial T}{\partial v_i}, \quad (515)$$

where the index i runs over both the particles and the three components of velocity i.e., for N particles, i runs from 1 to $3N$. (This is a rather trivial application of EHFT — be patient.)

But $\frac{\partial T}{\partial v_i}$ is just p_i , so

$$2T = \sum_i v_i p_i \quad (516)$$

$$= \sum_i \left[\frac{d}{dt} (r_i p_i) - r_i \frac{d}{dt} p_i \right]. \quad (517)$$

where we have used $v_i = \frac{d}{dt} r_i$ and the product rule for derivatives.

Now let us consider averaging over a long time duration. We'll use “bar”s to denote this “long time” average”. i.e., for a quantity A , its time average is

$$\bar{A} = \lim_{\tau \rightarrow \infty} \frac{\int_0^\tau A(t) dt}{\tau}. \quad (518)$$

If A is the derivative of a function which remains **bounded**¹¹², then $\bar{A} = 0$. To see this, write $A(t) = \frac{d}{dt} B(t)$ (where $B(t)$ is bounded):

$$\bar{A} = \lim_{\tau \rightarrow \infty} \frac{\int_0^\tau A(t) dt}{\tau} \quad (519)$$

$$= \lim_{\tau \rightarrow \infty} \frac{B(\tau) - B(0)}{\tau} \quad (520)$$

$$= 0 \quad \text{since } B \text{ is bounded.} \quad (521)$$

¹¹¹My treatment here is unoriginal. When I first prepared this section, I used as a reference: L. D. Landau and E. M. Lifshitz, *Mechanics*, 3. ed. (Elsevier, Butterworth Heinemann, Amsterdam, 2007).

¹¹²By B being *bounded*, we mean that there is exists an L , such that for all x , we have $|B(x)| \leq L$

E Stirling's approximation

So if we take the long time average of both sides of Eq. 517, and $\sum_i r_i p_i$ is bounded, then

$$2\bar{T} = -\overline{\sum_i r_i \frac{d}{dt} p_i}. \quad (522)$$

And if the forces on each particle may be derived from a potential V , then by Newton's 2nd law:

$$\frac{d}{dt} p_i = -\frac{\partial V}{\partial r_i} \quad (523)$$

so that Eq. 522 may be written as:

$$2\bar{T} = \overline{\sum_i r_i \frac{\partial V}{\partial r_i}}. \quad (524)$$

The quantity on the RHS is known as a **virial**.

If V is a positive homogeneous function of order k of all its position arguments, then EHFT may be applied to the quantity being averaged on the RHS of Eq. 524, giving the **virial theorem**:

$$\boxed{2\bar{T} = k\bar{V}}. \quad (525)$$

- for a gravitational interaction between particles (i.e., Eq. 508), V is a function of order -1 , and thus the virial theorem tells us that

$$\boxed{2\bar{T} = -\bar{V}} \quad \text{for a gravitationally bound system.} \quad (526)$$

This is the result required for SITP Problem 1.55, where it is written in the equivalent form $\bar{U}_{\text{potential}} = -2\bar{U}_{\text{kinetic}}$.

E Stirling's approximation (SITP B.3)

- Stirling's approximation deals with approximations for $n!$ or when n is large (e.g., for a large number of oscillators in the Einstein model).
- the treatment of SITP, Appendix B.3, pg 389, is pretty good – straight to the point. The result is the approximation:

$$n! \approx e^{n \ln n - n} \sqrt{2\pi n} \left(1 + \frac{1}{12n} + \dots \right) \quad (B.23)$$

Many times it's good enough just to use

$$n! \approx e^{n \ln n - n} \quad (527)$$

or equivalently, in a form that we will frequently use:

$$\ln n! \approx n \ln n - n. \quad (528)$$

E Stirling's approximation

- Stirling's approximation may be evaluated at non-integer values of n , and thus also allows one to evaluate the “derivative of the factorial”.

There is in fact an exact extension of factorial to real numbers known as the **Gamma function**:

$$\Gamma(x) := \int_0^\infty t^{x-1} e^{-t} dt \quad (529)$$

for all positive x , defined so that $n! = \Gamma(n+1)$. Obviously just agreeing with $n!$ at integer n is insufficient to *uniquely* define a suitable extension of the factorial function. However, the [Bohr-Mollerup theorem](#) states that a small set of additional constraints *do* define this extension uniquely.

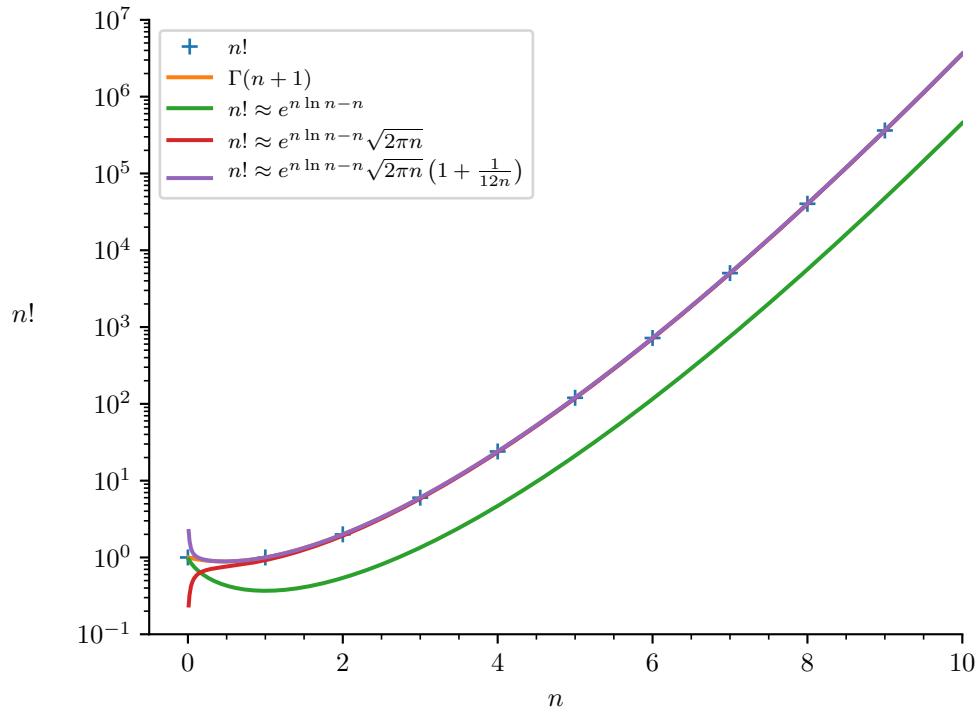


Figure 36: Accuracy of Stirling's approximation

- if you are interested in mathematical physics it's really worth understanding at least one of the (many) ways that Stirling's approximation is determined (i.e., the Gaussian of Fig. B.5 of SITP). Namely, [Laplace's method](#), which generalizes in a very useful way to the complex plane. (I wish someone had of told me this ... it has turned out to be pretty important for my research.)

F The volume of hypersphere in n -dimensions (SITP B.4)

- first let us make sure that we know what the problem is. We define the **volume of a hypersphere** of radius R in n -dimensions as being

$$V_n(R) = \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \dots \int_{-\infty}^{+\infty} dx_n f(\vec{x}) \quad (530)$$

where

$$f(\vec{x}) = \begin{cases} 1 & \text{if } x_1^2 + x_2^2 + \dots + x_n^2 < r^2 \\ 0 & \text{if } r^2 < x_1^2 + x_2^2 + \dots + x_n^2 \end{cases} \quad (531)$$

- note the familiar special cases

$$V_2(R) = \pi R^2 \quad \text{area of circle} \quad (532)$$

$$V_3(R) = \frac{4}{3}\pi R^3 \quad \text{volume of sphere} \quad (533)$$

It is not straightforward to generalize the specific techniques normally used to derive these to $n = 4$ and beyond. Instead, I will employ a general approach, suitable for arbitrary n (a more condensed presentation of this method is available in: J.-M. Lévy-Leblond, “N-Dimensional Variations on Themes of Pythagoras, Euclid, and Archimedes”, [The Mathematical Intelligencer 26, 43–53 \(2004\)](#)).

- based on $V_2(R)$ and $V_3(R)$ we might expect that $V_n(R)$ will be proportional to R^n . You may verify that this is the case by making the change of variables $x'_i = Rx_i$ for $i = 1$ to n in Eq. 530.
- the volume of hypersphere in n -dimensions can be found if we know the *surface* of a hypersphere in n -dimensions. Remember that the area of a circle and the volume of a sphere are quite easily determined when we know the circumference of a circle and surface area of circle respectively; i.e.,

$$V_2(R) = \int_0^R dr \underbrace{2\pi r}_{\text{circumference of a circle}} \quad (534)$$

$$= \pi R^2 \quad (535)$$

and

$$V_3(R) = \int_0^R dr \underbrace{4\pi r^2}_{\text{surface area of a sphere}} \quad (536)$$

$$= \frac{4}{3}\pi R^3 \quad (537)$$

from which we surmise

$$V_n(R) = \int_0^R dr S_n(r) \quad (538)$$

where $S_n(r)$ is the **surface area of a hypersphere** of dimension n and radius r , with the familiar special cases $S_2(r) = 2\pi r$ and $S_3(r) = 4\pi r^2$. Actually, we can view this expression as *defining* what we mean by the surface area of a hypersphere.

- instead of determining $V_n(R)$ directly, we will find $S_n(R)$ from which $V_n(R)$ follows readily. Note that since $V_n(R) \propto R^n$, it follows from Eq. 538 that $S_n(R) \propto R^{n-1}$.
- to motivate the approach that we will take to determine $S_n(R)$, consider a seemingly unrelated problem: what is the value of the integral

$$G = \int_{-\infty}^{+\infty} dx e^{-x^2} ? \quad (539)$$

Note that e^{-x^2} has no elementary anti-derivative. But there is a nice trick that you may have seen before: introduce a second coordinate y and instead of G consider G^2 :

$$G^2 = \int_{-\infty}^{+\infty} dx e^{-x^2} \int_{-\infty}^{+\infty} dy e^{-y^2} \quad (540)$$

$$= \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy e^{-(x^2+y^2)} \quad (541)$$

and now switch to polar coordinates, recognizing that the integrand only has an r (and not ϕ) dependence:

$$G^2 = \int_0^\infty dr 2\pi r e^{-r^2}. \quad (542)$$

This integral may be readily evaluated by standard techniques (change of variables $u = r^2$), unlike the integral in Eq. 539. We find that $G^2 = \pi$, and thus $G = \sqrt{\pi}$.

- note that in switching to polar coordinates we used the formula for the circumference of a circle (the “area of a hypersphere in $n = 2$ ”), so that Eq. 542 is of the form:

$$G^2 = \int_0^\infty dr S_2(r) e^{-r^2}. \quad (543)$$

Note that if knew G , and only knew that $S_2(r) \propto r$, we could determine $S_2(r)$ from this equation. That is pointless, since we *do* know $S_2(r)$, but the generalization of this idea works in n -dimensions (!):

$$G^n = \int_0^\infty dr S_n(r) e^{-r^2} \quad (544)$$

and writing $S_n(r) = \alpha_n r^{n-1}$ (where α_n is to be determined)

$$G^n = \int_0^\infty dr \alpha_n r^{n-1} e^{-r^2} \quad (545)$$

$$= \alpha_n \int_0^\infty dr r^{n-1} e^{-r^2}. \quad (546)$$

and making a change of variables $u = r^2$ gives:

$$G^n = \alpha_n \frac{1}{2} \int_0^\infty du u^{\frac{n}{2}-1} e^{-u}. \quad (547)$$

from which we recognize the definition of the gamma function (Eq. 529), so that we may rewrite as:

$$G^n = \frac{1}{2} \alpha_n \Gamma\left(\frac{n}{2}\right) \quad (548)$$

Recalling from the case of $n = 2$ that $G = \sqrt{\pi}$, we have:

$$\pi^{n/2} = \frac{1}{2} \alpha_n \Gamma\left(\frac{n}{2}\right) \quad (549)$$

which we may rearrange to give

$$\alpha_n = \frac{2\pi^{n/2}}{\Gamma\left(\frac{n}{2}\right)} \quad (550)$$

and thus the surface area of a hypersphere in n -dimensions is

$$S_n(R) = \frac{2\pi^{n/2}}{\Gamma\left(\frac{n}{2}\right)} R^{n-1} \quad (551)$$

And from Eq. 538, we obtain the volume of a hypersphere in n -dimensions:

$$V_n(R) = \frac{2\pi^{n/2}}{n\Gamma\left(\frac{n}{2}\right)} R^n \quad (552)$$

which may be rewritten using the identity $x\Gamma(x) = \Gamma(x+1)$ (analogous to $n(n-1)! = n!$) as:

$$V_n(R) = \frac{\pi^{n/2}}{\Gamma\left(\frac{n}{2} + 1\right)} R^n \quad (553)$$

G How to use CoolProp to obtain fluid properties

A collection of computer routines known as [CoolProp](#) allow one to obtain various fluid properties programmatically: e.g., the enthalpy of water as a function of temperature and pressure. The python interface is straightforward to use.

In professional work, computer programs such as CoolProp, have replaced tables (small excerpts of which are contained in SITP; e.g., Table 4.3 on page 140 of SITP). As always, be careful and seek independent means to check any results that you obtain. Computers allow one to obtain results more quickly than with tables. Sometimes though, it is *wrong* results that are obtained more quickly. For example, when preparing a figure in these notes showing the liquid-gas coexistence

region of N_2 , I incorrectly assumed that ' V ' was Coolprop's symbol for volume; instead the symbol ' V ' represents viscosity!

The best single link for documentation for the Python interface to CoolProp is:

<http://www.coolprop.org/coolprop/HighLevelAPI.html>.

If you want to use CoolProp on your own computer and installation of python, you will need to install it (i.e., `python3 -m pip install coolprop`)

Here is a [binder link](#) that will allow you to run some examples of using CoolProp in a browser *without* installing python and CoolProp. Please be patient, as it takes a bit of time to load (up to half a minute). If you are comfortable with running jupyter notebooks on your own computer, you can download the examples from:

https://github.com/jddmartin/coolprop_examples_binder_repo

H Comments on approximations and assumptions in problem solving

Some students *really* dislike a fraction of the problems in SITP. I have found that difficult to understand, because I have solved many of these problems and mostly found them to be interesting and worth my time.¹¹³

I think that I have figured out the reason for this discrepancy. Consider the following classification of physics problems:

- (1) problems which require the use of well-established techniques. The assumptions or required approximations (if any) are stated (e.g., "to first order in ..") or clearly implicit (e.g., non-relativistic approximations in mechanics). These problems are not necessarily easy — they may be difficult because they might require combining techniques in ingenious ways. (Think chess "combinations"!)
- (2) problems in which some approximations or assumptions *must* be made, but these are not stated. But there *is* an answer that can be obtained within a certain time. One might fall astray by making a sub-optimal approximation or assumption.
- (3) problems for which it is not known if there is an answer that can be obtained within a reasonable amount of time, either exactly, or using suitable approximations; i.e., most interesting research questions.

Problems of type 1 are found in many textbooks and courses, as they are useful for building skills. Students get used to them and like them. And they are also straightforward for instructors and TAs to mark.

Many SITP problems are of type 2 — valuable for gaining practice in solving *real* problems, for which no genie will sit on your shoulder, whispering suggested approximations and assumptions into your ear. To implicitly suggest that real-life problems are as well-defined as (most) textbook problems is a disservice.

¹¹³An example is SITP Problem 1.48. Similar considerations apply to some of the problems that I have composed.

I Comments on the “integration” of the isothermal compressibility, isobaric thermal expansivity, and similar quantities

To solve type 2 problems we must ask: what are relevant physical ideas (energy, entropy, ...)? If some information is missing (for a “rigorous” solution), what approximations or assumptions could you make to get any answer? What is the “best” solution given the information that you have? Are your approximations too drastic? Under what conditions would the assumptions be invalid? What further information would help improve your solution?

It is necessary to be flexible when marking student’s answers to type 2 problems. There may not be just “one true answer”. (Although often there is only one obvious route to an answer, given the information provided. That is mostly the case for the problems in SITP.)

I contend that practising physicists frequently need to solve type 2 problems and aspire to (and occasionally) solve type 3 problems. I also suspect that *mathematical* research is more aligned — at least in spirit — with type 2 and type 3 problems than many students appreciate; e.g., what hypotheses are needed to make progress?

I anticipate that my comments here will provoke further anger!

I Comments on the “integration” of the isothermal compressibility, isobaric thermal expansivity, and similar quantities

- the following comments are motivated by some student’s questions and comments regarding Problem 5.27(b) of SITP. (These comments also apply to Problem 1.7 of SITP and to “real life”.)
- the isothermal compressibility is defined as:

$$\kappa_T := -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T. \quad (554)$$

- when provided with a value of the isothermal compressibility at a particular pressure P_0 and temperature T , how should we calculate the change in volume with pressure, under constant temperature conditions?
- interpreting Eq. 554 as a differential equation gives the solution:

$$V = V_0 e^{-\kappa_T(P-P_0)}, \quad (555)$$

under the assumption that κ_T is independent of pressure. However, κ_T is *not* independent of pressure for any known material.

- so I argue that when provided with a value of κ_T , at a specific pressure P_0 , the first order expansion of Eq. 555, namely:

$$V \approx V_0 (1 - \kappa_T(P - P_0)), \quad (556)$$

is of the same order of accuracy as Eq. 555, as the latter neglects the pressure variation of κ_T , which typically gives comparable errors as the approximate solution (Eq. 556). Thus, this approximate solution is preferred due to its simplicity.

I Comments on the “integration” of the isothermal compressibility, isobaric thermal expansivity, and similar quantities

- as a straightforward illustration of the principles of my point, consider an ideal gas, as everything is known analytically. Specifically,

$$-\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{P} \quad (557)$$

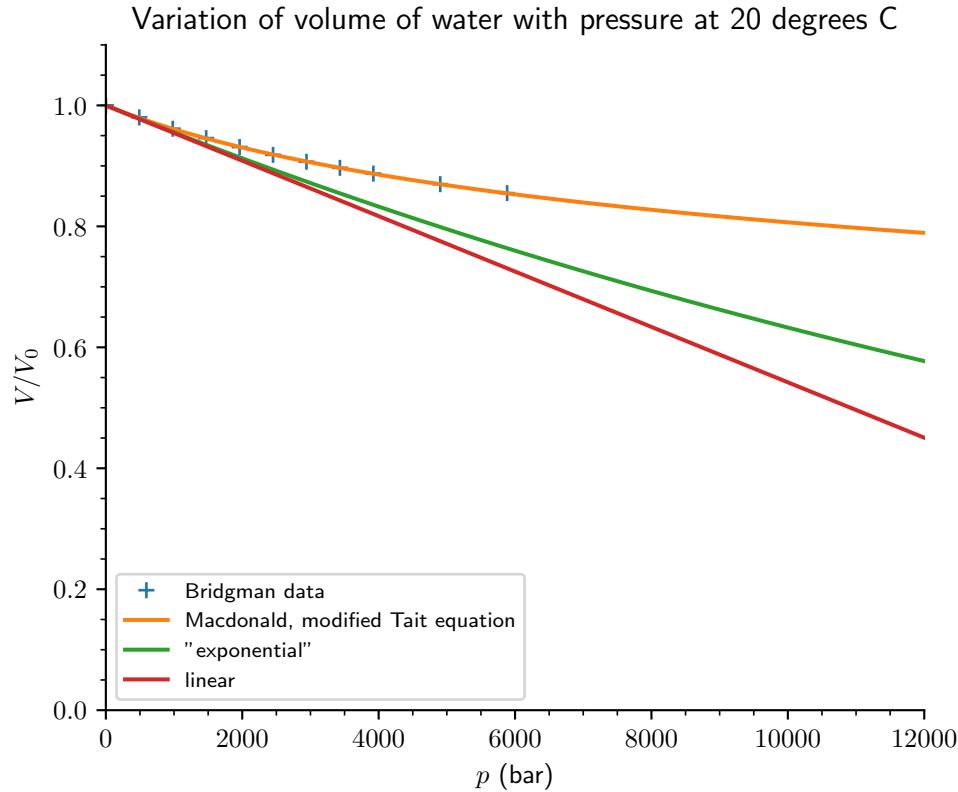
i.e., $\kappa_T = 1/P$.

- let’s compare the competing solutions for V/V_0 as a function of P with constant T , for the ideal gas ($\kappa_T = 1/P_0$):

method	V/V_0	expansion in $(P - P_0)/P_0$
exact solution	$\frac{P_0}{P}$	$\frac{V}{V_0} = \frac{1}{1 + \left(\frac{P - P_0}{P_0}\right)}$ $\approx 1 - \left(\frac{P - P_0}{P_0}\right) + \left(\frac{P - P_0}{P_0}\right)^2 + \dots$
exponential solution	$e^{-\frac{P - P_0}{P_0}}$	$\frac{V}{V_0} \approx 1 - \left(\frac{P - P_0}{P_0}\right) + \frac{1}{2} \left(\frac{P - P_0}{P_0}\right)^2 + \dots$
linear approximation	$1 - \left(\frac{P - P_0}{P_0}\right)$	$\frac{V}{V_0} = 1 - \left(\frac{P - P_0}{P_0}\right)$

- we see that the exact result, the exponential solution, and the linear approximation agree to first order in $(P - P_0)/P_0$, but all three disagree in the 2nd order.
- this example illustrates that — at least for the ideal gas — the use of the exponential solution (Eq. 555) over the linear approximation (Eq. 556) is unwarranted.
- of course most materials will not have the same simple pressure dependence of the isothermal compressibility as the ideal gas. Nonetheless, in general, the neglect of the pressure dependence of the isothermal compressibility corresponds to an error of 2nd order in $(P - P_0)/P_0$. For interest I have plotted water volume versus pressure at 20 °C using various models (please see source code for references):

<https://gist.github.com/jddmartin/000ebf44093a73fe1211dd97b534998b>).



- this plot illustrates that the improvement of the exponential solution over the linear approximation is marginal.
- so *why* is V in the denominator of our definition of κ_T (Eq. 554)? It is to make our characterization of isothermal compressibility behaviour *intensive*, i.e., not depend on the amount of material (see Section 7).
- similar considerations apply to the isobaric thermal expansivity:

$$\beta := \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (558)$$

i.e., $V \approx V_0 (1 + \beta(T - T_0))$ is the preferred expression if the temperature dependence of β is not given. Again, the purpose of the $1/V$ factor in Eq. 558 is to make β an intensive property of the material in question, i.e., independent of the amount of material.¹¹⁴

¹¹⁴One might imagine being given a temperature dependent β . Then computing the volume as a function of temperature would involve solving a differential equation (perhaps numerically using a computer). However, if β has a significant temperature dependence for a material, then it is likely that the material’s volume (normalized by the amount of material — say moles) would have been tabulated as a function of temperature, rendering integration unnecessary.

J The relationship between chemical potentials and the Gibbs free energy

(This section used to be in main body, but after some Phys 358 course reorganization, there is no longer time to cover this material in the lectures.)

- by $dG = -SdT + VdP + \mu dN$, we know that

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}. \quad (559)$$

- suppose that we have a system that can be described by T , P , and N .
- the quantity:

$$\frac{G(T, P, N)}{N}$$

must be intensive (see Section 7). An intensive quantity can be written as a function of other intensive quantities, and thus we know:

$$\frac{G(T, P, N)}{N} = f(T, P) \quad (560)$$

where f is some function. Rearranging gives:

$$G(T, P, N) = N f(T, P). \quad (561)$$

Substituting this into the RHS of Eq. 559 gives:

$$\mu(T, P) = f(T, P) \quad (562)$$

and thus by Eq. 561:

$$G(T, P, N) = N \mu(T, P) \quad (563)$$

- for a system with different types of particles, this result generalizes to:

$$G(T, P, N) = N_1 \mu_1 + N_2 \mu_2 + \dots \quad (564)$$

- for these mixtures μ_1 , μ_2 , etc..., depend on relative concentrations.

K Chemical potentials for ideal gases

(This section used to be in main body, but after some Phys 358 course reorganization, there is no longer time to cover this material.)

- from the entropy of an ideal monatomic gas (the Sackur-Tetrode equation), we can determine the corresponding chemical potential μ , directly from:

$$\mu := -T \left(\frac{\partial S}{\partial N} \right)_{V,U}. \quad (565)$$

K Chemical potentials for ideal gases

- however, the result that $G(T, P, N) = N\mu(T, P)$ allows μ to be computed for any — not just monatomic — ideal gas:

Rewriting as $\mu(T, P) = \frac{1}{N}G(T, P, N)$, we have

$$\left(\frac{\partial \mu(T, P)}{\partial P} \right)_T = \frac{1}{N} \left(\frac{\partial G}{\partial P} \right)_{T, N}. \quad (566)$$

From $dG = -SdT + VdP + \mu dN$, we have:

$$\left(\frac{\partial G}{\partial P} \right)_{T, N} = V. \quad (567)$$

Thus, we may write Eq. 566 as:

$$\left(\frac{\partial \mu(T, P)}{\partial P} \right)_T = \frac{1}{N}V \quad (568)$$

and using the ideal gas law

$$\left(\frac{\partial \mu(T, P)}{\partial P} \right)_T = \frac{kT}{P}. \quad (569)$$

This equation may be integrated under conditions of constant temperature, from a starting pressure P_0 to an arbitrary pressure P , to give:

$$\mu(T, P) - \mu(T, P_0) = kT \ln \left(\frac{P}{P_0} \right). \quad (570)$$

- thus if we know the chemical potential of an ideal gas at a given pressure and temperature, we may determine its chemical potential at another pressure, but the same temperature. It is customary to take $P_0 = 1$ bar and define:

$$\mu^\circ(T) := \mu(T, 1 \text{ bar}) \quad (571)$$

and write:

$$\mu(T, P) = \mu^\circ(T) + kT \ln \left(\frac{P}{P_0} \right) \quad (572)$$

where $\mu^\circ(T)$ may be supplied in tables. This result is required in SITP Problem 5.41.

L Remote course organization

I taught the UW course, Phys 358, three times during the pandemic, with some slight evolution in the course organization.

For posterity (but hopefully not another pandemic) I have included this appendix describing how the remote course was organized.

The Spring 2021 offering of Phys 358 at UW was composed of six two-week long modules. These modules corresponded to the following sections of the course notes:

- (1) (a) Mathematical prerequisites
 - (b) Liquid-in-glass thermometers
 - (c) Galilean thermometers and buoyancy
 - (d) Constant volume gas thermometers
 - (e) The absolute zero of temperature and the ideal gas law
 - (f) The relationship between temperature and energy for an ideal gas
 - (g) Constant pressure heat capacities and the 1st law of thermodynamics
 - (h) Intensive and extensive thermodynamic variables
- (2) (a) Expansion and compression work
 - (b) Introduction to phase transitions
 - (c) Enthalpy
- (3) (a) Thermal conductivity
 - (b) The Einstein solid model
 - (c) Two-state systems
- (4) (a) Monatomic ideal gases
 - (b) The 2nd law of thermodynamics
 - (c) The 3rd law of thermodynamics?
- (5) (a) Cyclic heat engines
 - (b) Interlude — Are *we* heat engines?
 - (c) Cyclic refrigerators
- (6) (a) Helmholtz free energy
 - (b) The available work interpretation of Helmholtz and Gibbs free energies
 - (c) Thermodynamics potentials — general considerations
 - (d) Gibbs free energy and the phase transitions of pure substances

N Physical reference data

- (e) The Clausius-Clapeyron relation
- (f) The relationship between chemical potentials and the Gibbs free energy
- (g) Chemical potentials for ideal gases
- (h) Macroscopic closing words

These sections correspond to the entirety of the first three Parts of these notes: I. Macroscopic phenomenological thermal physics, II. Entropy and temperature, and III. Macroscopic thermal physics with entropy and the second law.

The last part of these notes: IV. Thermal radiation and the temperature of the earth is not normally part of Phys 358, although I welcome your questions and comments either during the course or after it is complete.

M Extended example problems

These are currently in a separate document: [extended example problems](#)

N Physical reference data

I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of science, whatever the matter may be.

Lord Kelvin

N.1 Basic reference data

SITP contains a useful “Reference data” section at the end of the book (pg 402); this section is also available at: <http://physics.weber.edu/thermal/figures.pdf> (see the last four pages).

If you are enrolled in Phys 358, an enhanced version is available on Learn.

N.2 Open source alternatives

Some open source alternatives to some of the reference data are:

https://en.wikipedia.org/wiki/Periodic_table#Overview

https://en.wikipedia.org/wiki/Standard_Gibbs_free_energy_of_formation

https://en.wikipedia.org/wiki/Standard_enthalpy_of_formation#Examples:_standard_enthalpies_of_formation_at_25_%C2%B0C

N.3 Non-ideal fluid properties

For problems involving non-ideal fluids (the steam engine and refrigerator), SITP provides some tables of fluid properties. On the following pages I have reproduced his Tables 4.1, 4.2, 4.3, and 4.4 using the CoolProp software (see Appendix G). There are slight differences between the quantities as calculated by CoolProp and those tabulated in SITP, especially for HFC-134a. I am not sure which are more accurate, but the CoolProp generated tables have the advantage that they can easily be extended to different pressures, temperatures, and fluids. My code may be found at:

https://github.com/jddmartin/coolprop_to_make_sitp_tables

Reproduction of Table 4.1 of SITP using CoolProp: “*Properties of saturated water/steam. Pressures are given in bars, where 1 bar = 105 Pa ≈ 1 atm. All values are for 1 kg of fluid, and are measured relative to liquid water at the triple point (0.01 °C and 0.006 bar).*

T (°C)	P (bar)	H_{water} (kJ)	H_{steam} (kJ)	S_{water} (kJ/K)	S_{steam} (kJ/K)
0.0	0.006	-0	2501	-0.000	9.156
10.0	0.012	42	2519	0.151	8.900
20.0	0.023	84	2537	0.296	8.666
30.0	0.042	126	2556	0.437	8.452
50.0	0.124	209	2591	0.704	8.075
100.0	1.014	419	2676	1.307	7.354

Reproduction of Table 4.2 of SITP using CoolProp: “*Properties of superheated steam. All values are for 1 kg of fluid, and are measured relative to liquid water at the triple point.*

P (bar)	Temperature (°C)				
	200	300	400	500	600
1.0	H (kJ)	2875	3075	3279	3489
	S (kJ/K)	7.836	8.217	8.545	8.836
3.0	H (kJ)	2866	3070	3275	3487
	S (kJ/K)	7.313	7.704	8.035	8.327
10.0	H (kJ)	2828	3052	3264	3479
	S (kJ/K)	6.696	7.125	7.467	7.764
30.0	H (kJ)		2994	3232	3457
	S (kJ/K)		6.541	6.923	7.236
100.0	H (kJ)			3097	3375
	S (kJ/K)			6.214	6.599
300.0	H (kJ)			2153	3085
	S (kJ/K)			4.476	5.796

O Notes on sources

Reproduction of Table 4.3 of SITP using CoolProp, “*Properties of the refrigerant HFC-134a under saturated conditions (at its boiling point for each pressure). All values are for 1 kg of fluid, and are measured relative to an arbitrarily chosen reference state, the saturated liquid at –40°C.*”

P (bar)	T (°C)	H_{liquid} (kJ)	H_{gas} (kJ)	S_{liquid} (kJ/K)	S_{gas} (kJ/K)
1.0	-26.4	17	234	0.072	0.952
1.4	-18.8	27	239	0.111	0.945
2.0	-10.1	38	244	0.155	0.938
4.0	8.9	64	256	0.248	0.927
6.0	21.6	82	262	0.308	0.922
8.0	31.3	96	267	0.354	0.918
10.0	39.4	107	271	0.392	0.916
12.0	46.3	118	274	0.425	0.913

Reproduction of Table 4.4 of SITP using CoolProp, “*Properties of superheated (gaseous) refrigerant HFC-134a. All values are for 1 kg of fluid, and are measured relative to the same reference state as in Table 4.3.*”

P (bar)	Temperature (°C)			
	40	50	60	
8.0	H (kJ)	276	287	297
	S (kJ/K)	0.948	0.980	1.011
10.0	H (kJ)	272	283	293
	S (kJ/K)	0.918	0.953	0.985
12.0	H (kJ)		278	290
	S (kJ/K)		0.927	0.961

O Notes on sources

Mr. Beard is very courageous when he gives freely so many references to other books, because if a student ever did look at another book, I am sure he would not return again to continue reading Beard.

Feynman quoted in Gleick’s *Genius*

- (1) D. V. Schroeder, *An introduction to thermal physics* (Addison Wesley, San Francisco, CA, 2000) (SITP): the course textbook (on reserve at library).¹¹⁵ Errata are at: <http://physics.weber.edu/thermal/>. I follow the notation and conventions of this book and recommend that you have access to it. There is an [electronic version](#) (available through the [library](#) at UW).

I don’t think that you need anything other than SITP to do well in the course. However, if you have the time and inclination, there are other interesting books to look at.¹¹⁶ SITP has a *Suggested reading* section, which includes:

¹¹⁵Schroeder provides a useful perspective on teaching thermal physics [here](#) and also in a interview: <https://youtu.be/iJa06TV6gyg>.

¹¹⁶In consulting other references, please be aware of an inconsistency in the use of “adiabatic”, as noted in footnote 26 of these notes. Also, when assessing the relative merits of other books consider the [second textbook fallacy](#).

O Notes on sources

- (2) H. B. Callen, *Thermodynamics and an introduction to thermostatistics*, 2nd ed (Wiley, New York, 1985): a completely different point of view (more “axiomatic”). Some people prefer the [first edition](#) of this book for its focus.

An interesting older book that SITP recommends for experimental details is:

- (3) M. W. Zemansky, *Heat and thermodynamics; an intermediate textbook*, 5th edition (McGraw-Hill, New York, 1968) (available [here](#)). As SITP mentions, this 5th ed. is in some ways superior to later editions (one of which I first learned thermodynamics from).

SITP omits a long time student favourite:

- (4) Fermi, *Thermodynamics*: short, sweet and inexpensive (available [here](#)). Unfortunately Fermi’s notation is different from SITP and his units archaic. If you look beyond these issues, it is a wonderful book.

Since the publication of SITP, other high quality books have appeared, including:

- (5) S. J. Blundell and K. M. Blundell, *Concepts in thermal physics*, 2nd ed (Oxford University Press, Oxford ; New York, 2010): probably the single most useful alternative treatment to look at. There is an [electronic version](#) (available through the [library](#) at UW).

There are not just many books on statistical mechanics — there are many *good* books on statistical mechanics. Past students in Phys 358 have told me that they liked:

- (6) R. K. Pathria and P. D. Beale, *Statistical mechanics*, 3rd ed (Elsevier/Academic Press, Amsterdam ; Boston, 2011) (available [here](#)): The first chapter contains a more sophisticated discussion of much of Chapter’s 2 and 3 of SITP (Sackur-Tetrode etc...). This a good book to look at if you understand SITP, but are not fully satisfied with some of its explanations (but may not be the best choice for statistical mechanics in general). (Coincidentally, Pathria was a professor for many years at Waterloo.)

If you are interested in supplementary reading on the temperature of the earth (beyond what is necessary for Phys 358), I recommend:

- (7) F. W. Taylor, *Elementary Climate Physics*: you are now in an excellent position to study this book, which is written from a “physics” perspective.
- (8) R. T. Pierrehumbert, *Principles of Planetary Climate*: a more sophisticated treatment, again from a “physics” perspective. Fascinating.
- (9) Intergovernmental Panel on Climate Change, *Climate change 2013: The physical science basis* (<https://www.ipcc.ch/report/ar5/wg1/>): an extremely thorough summary of the science of climate change. This is probably the best place to “get started” on looking at any particular scientific aspect of climate change in detail as it provides copious references to the original literature. This is not light reading.

Compiling the preceding list has been a painful exercise in exclusion. I encourage you to contact me for book recommendations suited to your own interests and inclinations.

P About these notes

These notes complement Schroeder's, *Introduction to thermal physics* (SITP), the text that I have “required” when teaching Phys 358, *Thermal Physics*, at the University of Waterloo. If you are a student currently taking this course from me, then these notes are essential reading. This appendix is addressed to others, as here I provide some context and explain why these notes may be of interest to other instructors.

I have a high regard for SITP, especially the problems. As the organization of these notes indicates, I also admire the book's structure: an introduction to macroscopic phenomena (Ch. 1), a justification of entropy and temperature using microcanonical ensembles applied to specific systems (Ch.'s 2, 3), followed by an extensive study of the implications of the second law at the macroscopic level (Ch.'s 4, 5). The book then concludes with a more detailed study of statistical mechanics, including the canonical and grand canonical ensemble methods (Ch.'s 6-8). This sequence nicely matches up with the course structure here at Waterloo, where Physics students take Phys 358, *Thermal Physics*, in the first half of their third year. The [course calendar](#) describes the content:

Temperature and thermodynamic equilibrium. Work, internal energy and heat; first law, with examples. Kinetic theory of gases. Basic probability theory. Microscopic states and entropy. Absolute temperature, reversibility and the second law. Thermodynamic Functions and Maxwell's relations. Phase transitions. Third Law. Other applications of thermodynamics.

which matches Chapters 1 to 5 of SITP.

And in the second half of their third year they take Phys 359, *Statistical Mechanics*:

Fundamental postulate of statistical thermodynamics. Entropy. Microcanonical, canonical, and grand canonical ensembles. Fermi-Dirac, Bose-Einstein, and Boltzmann Statistics. Maxwell-Boltzmann velocity distribution. Applications to specific heat of solids, classical and quantum gases, electrons in metals, Planck's law of radiation, and Bose-Einstein condensation

which matches Chapters 6 to 7 of SITP. [117](#)

The intention is for the first course, Phys 358, to cover mainly thermodynamics, but to also contain *some* microscopic justification of the ideas of temperature and entropy. That nicely matches the “hybrid” approach of Chapters 1 to 5 of SITP.

So what about these notes? First and foremost they indicate how Chapters 2 and 3 of SITP can be cut down to the bare essentials. Specifically, $S := k \ln \Omega$ is introduced *at the same time* as the definition of temperature. It is a subjective matter, but without a laser-like focus on justifying the definition of temperature, the value of the “hybrid” approach may be diminished.

To the same end, I omit explicit treatment of the two-state paramagnet, using it as an example for students to work though, *after* they have studied the Einstein solid model, as I perceive no

¹¹⁷Recent offerings of Phys 359 have used SITP; prior offerings used R. K. Pathria and P. D. Beale, *Statistical mechanics*, 3rd ed (Elsevier/Academic Press, Amsterdam ; Boston, 2011).

Q Acknowledgements

significant advantages to studying the two-state paramagnet first.¹¹⁸

Of course, students can always consult SITP for more lengthy discussions, examples, and so on. To that end, with some minor, noted exceptions, I stick to the same notation, and indicate the corresponding sections of SITP (normally in section headings).

However Part IV of these notes, *Thermal radiation and the temperature of the earth*, deviates from SITP in a non-trivial way. Since students have gained familiarity with the Einstein solid as a byproduct of their study of Part II on temperature and entropy, they are able to follow Planck's original path of quantizing "material oscillators", Einstein's introduction of the photon, and thus the development of the theory of thermal radiation. In the normal sequence of study, thermal radiation appears later as an application of the general methods of statistical physics (e.g., Section 7.4 of SITP). But the importance of thermal radiation to our current predicament makes this "short-cut" (enabled somewhat by chance) worth considering.¹¹⁹ For example, at Waterloo not all students who take Phys 358 will continue with the follow-up Phys 359.

However, when preparing for the Spring 2020 offering of Phys 358 I realized — given our twelve week academic term at Waterloo — that Parts I-IV contain too much material for one term. Thus in the foreseeable future, I will not include Part IV in Phys 358; but I've decided to keep it in these notes, because 1) students may wish to study this material independently, and 2) somewhere else, someone else *may* be able to cover this material, or at least follow a similar strategy.

Finally, I do not intend to significantly lengthen the *main body* of these notes, reflecting my desire that Phys 358 students read them in their entirety. Instead I wish to continually refine and sharpen the main arguments based on reflection, experience and feedback.

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The Learn course page emoji  is from: <https://openmoji.org/library/#emoji=1F321>, licensed CC BY-SA 4.0.

¹¹⁸Filling in the details of the two-state paramagnet might be a good "flipped" classroom activity.

¹¹⁹Following Planck's path has the slight but undeniable advantage that it casts light on the genesis of one of the most important advances in physics. The early history of quantum mechanics has become somewhat inaccessible to students, whose textbooks take the expedient approach, ignoring Planck's tentative "material oscillators". Introductory quantum mechanics courses at the second year level can hardly discuss blackbody radiation at all, partially because students lack sufficient knowledge of electromagnetism, but more to the point, also thermal physics.

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