Acknowledgments

I acknowledge the Naval Academy Physics Department for helpful advice on the manuscript and on teaching in general. In particular, Professors Hartley, Huddle, Korman, Larsen, McIlhany, Morgan, Mungan and Tankersely have suggested problems, exercises and examples that are used in this book.
# Table of Contents

List of Tables ................................................. vii
List of Figures ................................................. ix
List of Symbols and Abbreviations ................................. x

Chapter 1  Introducing, $k_B T$ ................................. 1
  1.1  A Review of Temperature ................................. 2
    1.1.1  Absolute Temperature & Absolute Zero ............... 3
    1.1.2  Kinetic Energy & Temperature ......................... 5
    1.1.3  Equipartition of Energy ............................... 5
  1.2  Avagadro’s Number, Moles & Matter ........................ 9
    1.2.1  The Ideal Gas Law .................................. 10
    1.2.2  Equations of State .................................. 11
  1.3  Other Questions Answered by $k_B T$ ....................... 13

Chapter 2  What is Heat? ...................................... 15
  2.1  Heat Capacity and Latent Heat ............................. 16
    2.1.1  The Example of H$_2$O ................................ 18
    2.1.2  Microscopic Models for Heat Capacity .................. 20
  2.2  What is Entropy? ......................................... 25
    2.2.1  Adiabatic Gas Law ................................... 27

Chapter 3  Thermodynamics of Gases ............................. 31
  3.1  Isobaric Processes: $dP = 0$ ................................ 33
  3.2  Isentropic Processes: $dS = 0$ ................................ 34
  3.3  Isothermal Processes: $dT = 0$ ................................ 36
  3.4  Isometric Processes: $dV = 0$ ................................ 37
  3.5  The Carnot Heat Engine .................................... 38
    3.5.1  General Heat Engines .................................. 41

Chapter 4  Thermal Processes in Condensed Matter ............... 43
  4.1  Thermal Expansion ......................................... 45
  4.2  Isotropic Compression ...................................... 46
  4.3  Thermal Conduction ......................................... 47
  4.4  The Heat Equation .......................................... 51
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Thermal Radiation</td>
<td>56</td>
</tr>
<tr>
<td>5.1</td>
<td>Black Body Spectrum</td>
<td>57</td>
</tr>
<tr>
<td>5.2</td>
<td>Stefan-Boltzmann Law</td>
<td>59</td>
</tr>
<tr>
<td>5.3</td>
<td>Intensity of Thermal Radiation</td>
<td>62</td>
</tr>
<tr>
<td>Appendix A</td>
<td>Distributions &amp; the Boltzmann Factor</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>.1 The Boltzmann Factor</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>.2 Integration without Integrals</td>
<td>70</td>
</tr>
<tr>
<td>Author’s Biography</td>
<td></td>
<td>131</td>
</tr>
</tbody>
</table>
List of Tables
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Cooling behavior of a <em>nearly</em> ideal gas that liquefies at $-71^\circ$ C.</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>For a dilute gas of the above, with “frozen” bonds, we find that (a.) has $dof = 5$, while apparently (b.) and (c.) both have $dof = 6$.</td>
<td>8</td>
</tr>
<tr>
<td>1.3</td>
<td>P-V isotherms for (a.) hard spheres, (b.) Van der Waal’s fluid and (c.) Guldberg’s solid, Eqs. 1.10–1.12. $k_B T$ increases going up. A positive slope of $P$ vs. $V$ indicates a two-phase instability, i.e. a <em>phase transition</em>.</td>
<td>12</td>
</tr>
<tr>
<td>2.1</td>
<td>Heating. In each case, a quantity of heat $Q_{in}$ flows into a system, (a) at constant volume $V$, (b) at constant pressure $P$ and (c) during a <em>phase transition</em>.</td>
<td>15</td>
</tr>
<tr>
<td>2.2</td>
<td>Thermal properties of metals, air, water and other lab materials.</td>
<td>17</td>
</tr>
<tr>
<td>2.3</td>
<td>Heating water: 1 g of ice is heated from $-100^\circ$ C up to steam at $+100^\circ$ C under atmospheric conditions. The schematic phase diagram of water is inset. Notice that the proportions of specific heat are roughly as 9:18:6, similar to the $dof$ per-H$_2$O <em>molecule</em> described in Ch.1 footnotes [a,b,c].</td>
<td>19</td>
</tr>
<tr>
<td>2.4</td>
<td>Molar heat capacities for real gases: $C_V$ is plotted in units of $R$, the ideal gas constant. The grouping of similar molecules about half-integer values suggests $C_V \propto dof/2$ and $C_P - C_V = R$, per mole of molecules.</td>
<td>21</td>
</tr>
<tr>
<td>2.5</td>
<td>Einstein’s model for a solid.</td>
<td>23</td>
</tr>
<tr>
<td>2.6</td>
<td>Molar heat capacities for all monatomic solids, in units of $R$, are approximately equal to “3” under standard conditions.</td>
<td>24</td>
</tr>
<tr>
<td>2.7</td>
<td>$\gamma \equiv C_P/C_V$ for several molecular gases.</td>
<td>28</td>
</tr>
<tr>
<td>3.1</td>
<td>Would you recognize a 3d cow from this 2d cross-section?</td>
<td>32</td>
</tr>
<tr>
<td>3.2</td>
<td>$PV$ and $TS$ diagrams for an isobaric expansion of an ideal gas. Work done by the gas (blue) and heat inflow (orange) equal the shaded areas.</td>
<td>34</td>
</tr>
<tr>
<td>3.3</td>
<td>$PV$ and $TS$ diagrams for an isentropic/adiabatic expansion. Work done by the gas (blue) is equal to the shaded area under the curve.</td>
<td>35</td>
</tr>
</tbody>
</table>
3.4 *PV* and *TS* diagrams for an isothermal expansion of ideal gas. Work done *by* the gas (blue) and heat inflow (orange) equal the shaded areas. ...................................................... 36

3.5 *PV* and *TS* diagrams for an isometric heating of an ideal gas. Heat inflow (orange) equals the shaded area under the curve. 37

3.6 *PV* and *TS* diagrams for Carnot heat engines using ideal gas. Work done *by* the gas (blue) and heat inflow (orange) equal the shaded areas. ...................................................... 38

3.7 Carnot mass lifter using *hot* and *cold* reservoirs to do work. 39

4.1 Thermal and mechanical properties of condensed matter at STP. ........................................................................ 44

4.2 Conductivities of elemental solids at room temperature. . . 47

4.3 Thermal currents oppose the direction of the thermal gradient. 48

4.4 Flux of heat current *J* through a Gaussian surface surrounding a cylindrical heat source. ....................................... 49

4.5 Two identical blocks with initial temperatures differing by *ΔT* are joined along the *x* axis. They equilibrate to *T*<sub>avg</sub>, with the temperature profile varying in time and space as given by Eq. 4.10. .......................................................... 53

5.1 Planck’s law energy spectrum, from Eq. 5.1, and an infrared cat. ................................................................. 57

5.2 The “perceived” color and intensity of black-bodies at increasing temperature, as determined by Eq. 5.1. Intensities are renormalized to a linear temperature scale, e.g., as hot objects viewed through a welding helmet. The hottest objects, un-renormalized, would appear simply “white hot”. 58

5.3 Emissivities of poor (left) and good (right) black-body materials. ................................................................. 61

5.4 Example of the sun and the 1/(*d*)<sup>2</sup> fall-off of radiation intensity. 62

5.5 Schematic of the solar system (not to scale). Pluto is no planet. ................................................................. 63

6 A game of dice: what are the most frequent outcomes for rolling three dice so that they add to 8? .............................. 68
List of Symbols and Abbreviations

\( \langle \cdots \rangle \) Average, of Thermal Motion or Otherwise.

\( a \) Attraction Parameter [J m\(^3\)].

\( A \) Area [m\(^2\)].

\( b \) Excluded Volume per Particle [m\(^3\)].

\( b \) Bond Modes.

\( B \) Bulk Modulus [Pa].

\( c_p \) Specific Heat at Constant Pressure [J kg\(^{-1}\) K\(^{-1}\)].

\( c_v \) Specific Heat at Constant Volume [J kg\(^{-1}\) K\(^{-1}\)].

\( C_P \) Heat Capacity at Constant Pressure [J K\(^{-1}\)].

\( C_V \) Heat Capacity at Constant Volume [J K\(^{-1}\)].

\( d \) Dimensionality.

\( dof \) Degrees of Freedom.

\( e \) Electron Charge [ = 1.60 \times 10^{-19} \text{ C}] .

\( E \) Energy [J].
$f_B$ Boltzmann Factor [proportional to probability distribution].

$F$ Force [N].

$g$ Gravitational Acceleration \( = 9.80 \text{ m/s}^2 \) on Earth.

$h$ Height [m].

$h$ Planck’s Constant \( = 1.05 \times 10^{-34} \text{ J s} \).

$I$ Moment of Inertia \([\text{kg m}^2]\).

$k$ Spring Constant \([\text{N m}^{-1}]\).

$k_B$ Boltzmann’s Constant \(= 1.38 \times 10^{-23} \text{ JK}^{-1}\).

$k_B T$ Thermal Energy [J].

$KE$ Kinetic Energy [J].

$l$ Length of Bond or Spring [m].

$L_f$ Latent Heat of Fusion \([\text{J kg}^{-1}]\).

$L_v$ Latent Heat of Vaporization \([\text{J kg}^{-1}]\).

$m$ Molecular Mass \([\text{kg per-molecule}]\).

$M$ Total Mass \([\text{kg}]\).

$n$ Number of Moles \([\text{of molecules (or atoms) (or particles)}]\).

$N$ Number \([\text{of molecules (or atoms) (or particles)}]\).

$N_A$ Avagadro’s Number \(= 6.02 \times 10^{23]\).

$P$ Pressure \([\text{Pa}]\).
$PE$ Potential Energy [J].

$Q$ Heat [J].

$r$ Radius [m].

Rotational Modes.

$R$ Ideal Gas Constant [$= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$].

$S$ Entropy [J/K].

$T$ Absolute Temperature [K].

$U$ Internal Energy [J].

$v$ Velocity [m s$^{-1}$].

Vibrational Modes.

$V$ Volume [$m^3$].

$W$ Work [J].

$x, y, z$ Position [m].

$\alpha$ Thermal Expansion Coefficient [K$^{-1}$].

$\gamma$ Adiabatic Gas Constant.

$\Delta$ Change or Difference.

$\eta$ Thermal Efficiency.

$\kappa$ Thermal Conductivity [W m$^{-1}$ K$^{-1}$].

$\rho$ Number Density [kg m$^{-3}$].
\( \sigma_{SB} \) Stefan-Boltzmann Constant \([=5.67 \times 10^{-8} \text{J} \text{s}^{-1} \text{m}^{-2} \text{K}^{-4}]\).

\( \tau \) Mean Collision Time \([\text{s}]\).

\( \omega \) Angular Frequency \([\text{rad} \text{s}^{-1}]\).
Chapter 1

Introducing, $k_B T$.

Pronounced \(kā ˌtē\), $k_B T$ is a measure of the energy that is typical for thermal motion at the molecular (or atomic) (or particle) scale for a given, equilibrium absolute temperature $T$. It tells us, roughly, that the average kinetic energy of an individual molecule (or atom) (or particle) will be of the same order of magnitude as the natural thermal energy unit $k_B T$. For a given system there is an explicit connection between mechanical energies and $k_B T$. For example, a gas of atoms in equilibrium has an average kinetic energy per-atom of

$$
\langle KE_{atom} \rangle = \frac{3}{2} k_B T.
$$

(1.1)

Thermal equilibrium means that all parts of the system are at roughly the same temperature and in energy balance, while the other mysterious factors of $3/2$ and $k_B$ will be the focus of this Chapter. Suffice it to say, $3/2$ has to do with the space that a gas occupies and that it is 3-dimensional.

$k_B T$ is necessarily a post-20$^{th}$ century concept. We haven’t discussed temperature, generically indicated by “$T$”, but it appeals, basically, to our human senses of hot and cold. But what are hot and cold? We have learned that our bodies are made of cells and that certain channels controlling the flow of ions can open or close when the temperature is high or low. These
senses therefore have a microscopic and molecular origin. Also, these senses can be fooled: consider an “icy” menthol liniment rub for sore muscles or a “hot” pepper. Can we really trust our intuition for temperature?

To get to the bottom of this we will first review the historical definition of temperature and show that it relates to a modern viewpoint of energy and the now-known constituent parts that makeup our universe. We will find that $k_B T$ plays a role in thermal processes much the same as that played by the gravitational acceleration $g$ in freshman mechanics: it sets the scale for what can happen, and it makes an appearance in almost every calculation.

### 1.1 A Review of Temperature

The *de facto* standard for temperature, within the United States, is the *Fahrenheit* scale: $0^\circ F$ is a cold day, $100^\circ F$ a hot day, water freezes at $32^\circ F$.

Meanwhile the scale most widely-used outside of the U.S. and the most convenient for calculations in chemistry and engineering is the *Celsius* temperature scale: water freezes at $0^\circ C$, room temperature is $20^\circ C$, and water boils at $100^\circ C$. The intuitive advantage of this scale is that it is completely based on water, the ubiquitous substance that covers most of our Earth’s surface and makes up most of our bodyweight. In the lab, a Celsius thermometer is always available, and conversion factors are readily available:

\[
[\circ F] = [\circ C] \times \frac{9}{5} + 32,
\]

\[
[\circ C] = ([\circ F] - 32) \times \frac{5}{9}.
\]

Please note, however, that the temperature scales in these formulae are NEVER the correct “$T$” that is represented in the expression “$k_B T$”!
Figure 1.1: Cooling behavior of a nearly ideal gas that liquifies at $-71^\circ$ C.

We want to reserve “$T$” for representing quantities that are proportional to the average kinetic energy. But so far all of our temperature scales have allowed negative numbers, which in no sense could represent a kinetic energy. The reason that our first two temperature scales failed is that they are relative to an arbitrary zero: a cold day and freezing water. Why not freezing Helium? Or the temperature of a dilute gas isolated in deep space? The best choice is to set the zero of our temperature scale to the coldest possible temperature.

1.1.1 Absolute Temperature & Absolute Zero

Advances in experimental, low-temperature physics have confirmed this fact: No one has ever cooled matter below $\text{ABSOLUTE ZERO} = -273.15^\circ$ C. However, scientists come daily to within the smallest degree fractions of achieving absolute zero. The fact of absolute zero is convincingly proved for almost any gas by examining its volume versus temperature behavior at a constant pressure (Fig. 1.1) and extrapolating its collapse to zero volume at
absolute zero. If we subtract absolute zero from any Celsius temperature, we arrive at the Kelvin absolute temperature. It will suffice for \( k_B T \) to always use Kelvin temperature units:

\[
T[K] = \left[ ^\circ \text{C}\right] - (-273.15 ^\circ \text{C}).
\]

A few useful (approximate) Kelvin temperatures are:

0 K, Absolute Zero.
3 K, Temperature of Deep Space.
4 K, Helium Liquifies.
7 K, Lead becomes a Superconductor.
44 K, Surface Temperature on Pluto.
77 K, Nitrogen Liquifies.
150 K, approximate highest temperature superconductors.
273 K, Freezing Point of Water.
293 K, Standard Room Temperature.
300 K, Physicist’s “Convenient” Room Temperature. \((k_B T = 1/40 \text{ eV})\)
373 K, Boiling Point of Water.
740 K, Surface Temperature on Venus.
1200 K, Wood Fire.
1800 K, Melting Point of Iron.
4000 K, Melting Points of Diamond and Graphite.
5700 K, Earth’s Inner Core / Surface of Sun.
\(\sim 10^5\) K, Atomic Bomb.
\(\sim 10^6\) K, Corona of Sun / Magnetically Confined Plasma.
\(\sim 10^9\) K, Early Universe.
\(\sim 10^{12}\) K, Theoretical Temperature of Quark-Gluon Plasma.
\(\sim 10^{32}\) K, The Planck Temperature, \(k_B T = \sqrt{\hbar c^5/G}\).
1.1.2 Kinetic Energy & Temperature

All along the importance of temperature as the kinetic energy of a molecule (or atom) (or particle) has been emphasized. So why not just measure and report $T$ in ordinary energy units and call it a kinetic energy? Well it turns out that this would be ambiguous. The subtle difficulty with thinking of $k_B T$ as a kinetic energy is that the definition changes with different systems, e.g. water versus hydrogen, having different numbers of atoms per molecule, different geometries and different contributions to their kinetic energy! If you recall, an object sliding frictionlessly down a hill gets to the bottom quicker and is going faster than if it were an object rolling down a hill. The total kinetic energy at the bottom of the hill must be the same because of conservation of energy, but allowing additional channels for energy flow, namely rolling, has changed the nature of the motion. The same is true for temperature: it’s very definition depends on microscopic detail.

Notwithstanding the subtleties, an unambiguous definition for $k_B T$ does exist. Proposed by Boltzmann in 1877, $k_B$ had apparently no value assigned to it at the time, but was proposed rather as a theoretical ratio of atomic energies [in J] to their macroscopic temperatures [in K]. It was a conceptual tool if anything. Planck, however, determined a precise value for $k_B$ later on, in 1901, by fitting the law of black-body radiation:

$$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}.$$ \hfill (1.3)

1.1.3 Equipartition of Energy

We are now ready to relate $k_B T$ to all atomic and molecular energies. We use the approach known as equipartition, which states that on-average a
system with many *degrees of freedom*, meaning the number of mechanical
variables needed to uniquely specify its state, will have an amount of energy
\( \frac{1}{2} k_{B} T \) associated with each of its *quadratic* degrees of freedom. Here is
the most general example: A completely asymmetric molecule interacts with
its neighbors in a crystal. It translates with velocity (in three dimensions),
rotates (about three axes) and vibrates (about equilibrium). The molecule
also has *internal* vibration (along its bonds) if the temperature is high enough
to excite them. We calculate the average molecular energy \( E \) for this body
of mass \( m \), moments-of-inertia \( I \), and crystal spring constants \( k \) as:

\[
\langle E \rangle = \frac{1}{2} \langle m v_{x}^{2} \rangle + \frac{1}{2} \langle m v_{y}^{2} \rangle + \frac{1}{2} \langle m v_{z}^{2} \rangle \quad \leftrightarrow \text{translation in } d \text{ dimensions}
\]

\[
+ \frac{1}{2} \langle I_{1} \omega_{1}^{2} \rangle + \frac{1}{2} \langle I_{2} \omega_{2}^{2} \rangle + \frac{1}{2} \langle I_{3} \omega_{3}^{2} \rangle \quad \leftrightarrow \text{rotation about } \theta \text{ axes}
\]

\[
+ \frac{1}{2} \langle k x^{2} \rangle + \frac{1}{2} \langle k y^{2} \rangle + \frac{1}{2} \langle k z^{2} \rangle \quad \leftrightarrow \text{vibration along } \nu \text{ crystal axes}
\]

\[
+ \frac{1}{2} \langle m_{1} v_{1}^{2} \rangle + \frac{1}{2} \langle k_{1} l_{1}^{2} \rangle + \cdots \quad \text{and along } b \text{ “active” bonds (high-} T \rangle
\]

\[
= \frac{1}{2} k_{B} T \quad + \frac{1}{2} k_{B} T \quad + \frac{1}{2} k_{B} T
\]

\[
+ \frac{1}{2} k_{B} T \quad + \frac{1}{2} k_{B} T \quad + \frac{1}{2} k_{B} T
\]

\[
+ \frac{1}{2} k_{B} T \quad + \frac{1}{2} k_{B} T \quad + \frac{1}{2} k_{B} T
\]

\[
+ \frac{1}{2} k_{B} T \quad + \frac{1}{2} k_{B} T \quad + \cdots \quad \text{(see Appendix A)}
\]

\[
= \frac{1}{2} (d + \nu + 2) k_{B} T + b k_{B} T \quad , \quad \text{in thermal equilibrium. \quad (1.4)}
\]

The bottom line is that Eq. 1.4 makes sense from a chemical point of view:
if bonds or other modes are allowed to “turn on”, as it were, then there are
more ways for the molecules to *soak up* energy, via equipartition, so it actually
becomes more difficult to increase the temperature of complex molecules:
In equipartition, active quadratic degrees of freedom get $\frac{1}{2} k_B T$ of energy.

Notice that no mechanical parameters affect this energy; it is only necessary that the variable-dependence be quadratic (see Appendix A). A lucky coincidence is that translation, rotation and vibration are all quadratic. For a box of $N$ molecules, described by any portion of Eq. 1.4, we get $N$ contributions like this, so the total internal energy $U$ of the box is

$$U \equiv N\langle E \rangle \simeq \frac{\text{dof}}{2} N k_B T,$$

where $\text{dof} \equiv d + \mathcal{v} + \mathcal{r} + \ldots$ for all allowed modes.

Taking this a bit further,

1. **Gases** exhibit weak intermolecular forces, so all spring constants $k$ in Eq. 1.4 are zero, and bond forces are “frozen out”.\(^a\) Also rotations count only if they affect some reorientation. [$\text{dof} = d + \mathcal{v}$, per molecule]

2. **Liquids** behave roughly as a collection of rotating and vibrating molecules, attached to one another by springs.\(^b\) [$\text{dof} = d + \mathcal{v} + \mathcal{r}$, per molecule]

3. **Solids** at high temperatures may be modeled as a collection of atoms attached to a crystalline lattice by springs.\(^c\) [$\text{dof} = d + \mathcal{v}$, per atom]

In principle the $\text{dof}$ can depend on complexity, shape, symmetry, dimensionality and phase of matter. Test your intuition for $\text{dof}$ by studying Fig. 1.2. In each case, you should be able to identify the specific modes of motion that contribute. If you agree with the caption, then consider the most important examples that follow, which are based on symmetry:

\(^a\)H₂O steam is an exception. Only for $T$ very near 100° C and at low pressure are the bonds inactive; otherwise consult engineering “steam tables” [$\text{dof} \geq 6$ per molecule].

\(^b\)H₂O water is an exception. Water is denser than ice near melting, so it behaves with respect to thermal properties more like the solid described above. [$\text{dof} \simeq 6$ per atom].

\(^c\)H₂O ice is an exception. It is less dense than water, allowing orientational freedom, and so its molecules (rather than atoms) vibrate and may rotate [$\text{dof} \simeq 9$ per molecule].
Figure 1.2: For a dilute gas of the above, with “frozen” bonds, we find that
(a.) has $dof = 5$, while apparently (b.) and (c.) both have $dof = 6$. 
1. A point-like atom receives no rotational energy contributions of $1/2 k_B T$ since its rotation is indistinct. No angles at all describe its motion.

\[ dof = 3 \]

2. Linear molecules receive two rotational energy contributions of $1/2 k_B T$ since they have two distinct rotation axes, each requiring an angle.

\[ dof = 5 \]

3. Nonlinear molecules receive three rotational contributions of $1/2 k_B T$ since they have three distinct rotation axes, requiring three angles.

\[ dof = 6 \]

It can be confusing, at first, to count a molecule’s degrees of freedom. However the overarching principle is simple: There are some number of numbers that are required to completely describe a given system at any instant in time, and the total quantity of those numbers gives its degrees of freedom:

\[ dof = \text{number of numbers required to completely specify a system’s state.} \]

The only approximations in equipartition are: (1) the degrees of freedom must be quadratic, (2) the system must be allowed to equilibrate for a long time (perhaps forever) to populate all of the forms of motion with $1/2 k_B T$, and (3) even after a long time there are still, doubtless, fluctuations that disobey equipartition, even though the average of these should be but a small contribution to the larger energy, which leads us to moles.

### 1.2 Avagadro’s Number, Moles & Matter

The value of $k_B$ in Eq. 1.3 is exceedingly small in SI units, owing of course to atomic and molecular energies being very small for reasonable temperatures. For that reason, many chemists and engineers prefer to work in terms of the
molar energies of atoms or molecules. 1 mol is the large amount expressed by *Avagadro’s number*,

\[ N_A = 6.02 \times 10^{23}. \]  

(1.6)

A number \( N_A \) of gaseous atoms would fill 22.4 L of volume, at standard temperature and pressure, and also would have \( A \) grams of mass, with \( A \) being that gas’ *atomic mass number*. The symbol \( n \) is typically used for the number of moles, versus \( N \) for the actual number of a substance so that:

\[ N = nN_A. \]  

(1.7)

We shall use both of Eqs. 1.6–1.7 frequently in calculations on atoms, molecules, solids, liquids and gases: the constituents of matter. The numerical values make a rigid connection between the most microscopic and macroscopic (everyday object) length and energy scales.

### 1.2.1 The Ideal Gas Law

We shall pre-suppose that in freshman chemistry, everyone learns that the pressure \( P \), the volume \( V \), the number of molecules \( N \) and the temperature \( T \) are all related under the assumptions of an *ideal* gas via the *ideal gas law*:

\[ PV = Nk_B T. \]  

(1.8)

An ideal gas is one in which the constituents do not interact at all. It is a quite good approximation for gasses at low number density (\( \rho \equiv N/V \)). Actually, most readers likely recall the more common expression, \( PV = nRT \), wherein the definition of the mole in Eq. 1.7 is used and establishes a clear
definition of the chemist’s “Universal Gas” constant:

\[ R \equiv N_A k_B = 8.31 \text{ J K}^{-1}\text{mol}^{-1}. \tag{1.9} \]

### 1.2.2 Equations of State

Beyond the ideal gas law, when a gas becomes too dense or under too much pressure, or (worse) when the gas becomes a liquid or a solid, there are profound deviations from the ideal gas law. These deviations are energetic “corrections” with respect to the pressure: \( PV = N(k_B T + AP + BP^2 + \ldots) \) for gas-dependent parameters \( A, B, \) etc. The *number density* \( \rho \equiv N/V \) can also be used in place of pressure. A function relating \( P, V, T \) and \( N \) is called an *equation of state*. Here are a few that mimic phases of matter (Fig. 1.3):

1. **Gas of hard spheres** (BB’s) with a volume-per-sphere of roughly “\( b \)”,

\[
PV = N (k_B T + bP), \tag{1.10}
\]

2. **Van der Waal’s fluid** similar to Eq. 1.10 but with an attraction “\( a \)”,

\[
PV = N \left( k_B T + bP - a\rho + ab\rho^2 \right), \tag{1.11}
\]

3. **Guldberg’s solid** with “ideal” volume \( V_0 \) and thermal expansivity \( \alpha_0 \),

\[
PV = N \left( k_B T + k_B \alpha_0^{-1} (1 - V/V_0) \right). \tag{1.12}
\]
Figure 1.3: P-V isotherms for (a.) hard spheres, (b.) Van der Waal’s fluid and (c.) Guldberg’s solid, Eqs. 1.10–1.12. $k_B T$ increases going up. A positive slope of $P$ vs. $V$ indicates a two-phase instability, i.e. a phase transition.
1.3 Other Questions Answered by $k_B T$

Finally I wish to illustrate the ubiquitous presence of $k_B T$ in science and engineering. No proofs are given, as they are mostly beyond our scope. Please do, however, admire the breadth and simplicity of these results:

1. Our whole universe was in a hot dense state. Below a temperature $T$ electron/positron pair-production ceased because $2 m_e c^2 > k_B T$.

2. A portion of a galaxy is estimated to have a local temperature of $T$, as evidenced by its emitted photons having an average energy of $k_B T$.

3. The thickness of Earth’s atmosphere equals (roughly) the height $h$ at which a typical molecule’s potential energy $mgh$ equals $k_B T$.

4. The persistence length of DNA, i.e. its floppiness compared to (say) $1.5 \text{ cm}$ for spaghetti, is equal to its bending “rigidity” divided by $k_B T$.

5. A very dilute gas will always have a pressure-to-density ratio of $k_B T$.

6. If a reaction occurs only above a temperature $T$, then the activation energy barrier per molecule is likely to be on the order of $k_B T$.

7. An unbiased $p-n$ semiconductor junction naturally develops a thermal voltage across it equaling the inverse charge $e^{-1}$ times $k_B T$.

8. A 1D polymer-chain has an “entropic” spring-constant equal to its [total length $\times$ segment length]$^{-1}$ times $k_B T$.

9. In atomic collisions, the excitation energy of one atom can be resonantly transferred to another if the level differences match to within $k_B T$.

10. A black hole’s temperature $T$ is estimable from its local acceleration $g$, the speed of light $c$, and Planck’s constant $h$, by setting $h g/2\pi c = k_B T$. 

13
1. Sea water: A temperature of 39° F prevails throughout most of the deep sea. Express this temperature in °C and Kelvin units.

2. Absolute zero: Express absolute zero in °F.

3. Degrees of freedom: How many degrees of freedom does a bicycle have?

4. Equipartition: What are the average molecular energies of gases composed of (a) molecular Hydrogen and (b) Methane at \( T = 300K \)?

5. Moles: How many moles of water molecules are in the typical human body?

6. Ideal gas: One mole of an ideal gas at room temperature and atmospheric pressure (\( P_{atm} \approx 10^5 \text{ Pa} \)) is found experimentally to occupy a volume of 24 L. Use this to estimate \( k_B T_{room} \) in two units: \([J]\) and \([eV]\).

7. Van der Waals fluid: Re-plot Fig. 1.3(b) by your own means choosing some parameters for Eq. 1.11. Indicate, by shading, where all regions of phase-instability occur, as evidenced by positive \( P \) vs. \( V \) slope. Why would a positive slope be unstable?

8. Atmospheric composition: Using Equipartition, calculate the “rms” molecular speeds \( \sqrt{\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle} \) of (a) H\(_2\), (b) He, (c) O\(_2\) gases at room temperature. Compare to the escape velocity of Earth.

9. Integration without integrals: Using techniques from Appendix A calculate \( \langle x \rangle \) and the standard deviation of \( x \) with respect to \( \langle x \rangle \), for the distribution functions and domains, (a) \( f \sim e^{-x/\lambda}, \ 0 \leq x < \infty \) and (b) \( f \sim e^{-x^2/2\sigma^2}, \ (-\infty \leq x < \infty) \).
Chapter 2

What is Heat?

Heat is a flow of thermal energy. It affects more than just temperature, as it can also cause a change in pressure or volume, or a change in material phase, during which the temperature may not change at all. This is illustrated for three cases in Fig. 2.1. One must consider that, from the start, different experimental conditions will channel a given quantity of heat $Q$ into different modes of energy. Also, the energy that is created by heat is truly random, meaning that heat gets distributed equally among the degrees of freedom, namely, vibrations, rotations and translations. Heat can also mix ordered species into disordered arrangements. Most importantly, heat flows spontaneously from hot to cold, not vice versa.

![Figure 2.1: Heating. In each case, a quantity of heat $Q_m$ flows into a system, (a) at constant volume $V$, (b) at constant pressure $P$ and (c) during a phase transition.](image)
2.1 Heat Capacity and Latent Heat

As a first example, the constant-pressure vessel in Fig. 2.1(a) has an inflow of heat $Q$, that causes a rise in temperature, as well as pressure. The change in temperature $\Delta T$ in this case is proportional to the heat, via

\[ Q = C_V \Delta T, \]  

(2.1)

where $C_V$ is the heat capacity at constant volume [in J/°C]. The change in pressure is proportional as well but is found from the equation of state.

Similarly, for the constant pressure cylinder in Fig. 2.1(b), heat causes the temperature and volume to rise in proportion to the heat,

\[ Q = C_P \Delta T, \]  

(2.2)

where $C_P$ is the heat capacity at constant pressure [in J/°C]. The proportional change in volume is again found from the equation of state.

Finally, for a phase transition as in Fig. 2.1(c), there is no change in temperature. The material remains, ideally, at a constant configuration of $P, V, T$ until the entirety of its mass $M$ has been converted into a new phase. This implies the definition of the so-called latent heat $L$ [in J/kg], which is the positive energy-per-unit-mass associated with a phase transition:

\[ Q = ML. \]  

(2.3)

Heat capacity and latent heat data, along with the melting and boiling temperatures $T_m$ and $T_b$, are listed in Table 2.2 for many materials, including cryogenic liquids.
More often the value of $C_P$ is the relevant heat capacity for experiments, because it is more interesting than $C_V$, which is only for “sealed containers”, and the two definitions only differ noticeably for gases. The larger issue is their proportionality to “amount of stuff” $M$, which can be removed by defining their related specific heats $c_p$ and $c_v$:

$$C_P = M c_p$$

$$C_V = M c_v.$$  \hspace{1cm} (2.4)

The specific heats are constant per-gram heat capacities for each material, as in Table 2.2. In terms of a given, tabulated specific heat “c”, the heat capacity relations in Eqs. 2.1 and 2.2 become

$$Q = M c \Delta T.$$  \hspace{1cm} (2.5)
2.1.1 The Example of H$_2$O

The most important material in any science or engineering study is water. It covers everything. Even surfaces that appear dry often have an invisible monolayer of honeycombed water molecules covering them. We live on a water planet, so it is natural that our first inclination is to reference every other material to water. In fact, the original studies of heat did not consider it as an energy at all but rather as a fluid of some substance, called “caloric”, which carries heat. The unit of caloric, \(1 \text{ calorie} \ [\text{cal}] = 4.186 \text{ J}\), is the heat required to increase the temperature of 1 gram of water by 1° C. It is still often useful to work in units of calories, especially when working with water because its specific heats and latent heats are nice round numbers and fractions as shown in Fig. 2.3. The example in the figure shows how heating 1 g of ice, which is approximately 1 cm$^3$, happens by 5 additive steps:

+ 50 cal to heat ice initially at -100° C up to ice at 0° C,
+ 80 cal to melt all of the 0° C ice into cold water,
+ 100 cal to raise the resulting cold water up to its boiling point,
+ 540 cal to vaporize all of the boiling water into steam,
+ 33 cal to heat the resulting steam up to +200° C.

The net heat required for the whole process is about 800 cal, which is roughly half the “food energy” contained in a tic-tac, the tiny breath-mint. Since one “food” calorie is equal to 1000 “chemistry” calories, and a big meal might be 500 calories altogether, the total food energy that could be extracted and converted into heat from a big meal is enough to melt nearly 6.25 kg of ice, which is almost a 20 cm $\times$ 20 cm $\times$ 20 cm block!

WARNING: Hugging ice blocks is not a recommended weight-loss method.
Figure 2.3: Heating water: 1 g of ice is heated from -100° C up to steam at +100° C under atmospheric conditions. The schematic phase diagram of water is inset. Notice that the proportions of specific heat are roughly as 9:18:6, similar to the dof per-H$_2$O molecule described in Ch.1 footnotes [a,b,c].
2.1.2 Microscopic Models for Heat Capacity

It was already pointed out, in the caption of Fig. 2.3, that the \( \text{dof} \) have some relationship with the heat capacity and specific heats of matter. Roughly speaking, a system with more active degrees of freedom will tend to have a higher heat capacity than another system with equal numbers of atoms or molecules but fewer active degrees of freedom. The reason for this is simple; more degrees of freedom means more mechanisms to soak up and absorb energy, which makes for a higher heat capacity per-molecule. However, the argument is approximate because of the delicate nature of “active” degrees of freedom (see footnotes [a,b,c] on H\(_2\)O in Ch.1).

Gases

The easiest case is a box of \( N \) dilute molecules of a gas as in Fig. 2.1(a). The molecules have \( d \) translational and \( z \) rotational \( \text{dof} \) and strike the walls elastically, so the total internal energy \( U \) is conserved. Using Eq. 1.5 with \( \text{dof} = d + z \), we find \( U_{\text{gas}} \approx \frac{1}{2} (d + z) Nk_B T \). If the box is sealed, any change in \( U \) must be due to heat, i.e. \( dU = U'dT = dQ_{\text{in}} \); we conclude that the coefficient of \( dT \) must be equal to \( C_V \):

\[
C_{V,\text{gas}} \equiv \frac{dU}{dT} \approx \frac{\text{dof}}{2} Nk_B ,
\]

or for \( N = N_A \) molecules, we can use Eq. 1.9 to find the molar heat capacity:

\[
C_{V,\text{gas}} \approx \frac{\text{dof}}{2} R \text{ (per mole of gas molecules)} .
\]

Notice that the answer depends on the \( \text{dof} \) explicitly; i.e. in units of “\( R \)”, \( C_V \propto \text{dof}/2 \). To see how well this applies to real gases, see Fig. 2.4.
Figure 2.4: Molar heat capacities for real gases: $C_V$ is plotted in units of $R$, the ideal gas constant. The grouping of similar molecules about half-integer values suggests $C_V \propto dof/2$ and $C_P - C_V = R$, per mole of molecules.
The constant pressure heat capacity $C_P$ is always larger than $C_V$ because maintaining a gas’s pressure under constant heat requires work to expand its container, or else the gas’s pressure increases. As a result $dQ_{in}$ must supply an additional “$P\,dV$” work done by pressure on the container. When $Fdx$ work is done to move the piston in Fig. 2.1(b), we can equate that work to the “$P\,dV$” work, via the ideal gas law: $F\,dx = (F/A)A\,dx \equiv P\,dV = Nk_BdT$. Hence $dQ_{in} = dU + PdV = C_VdT + Nk_BdT$, and the coefficient of $dT$ gives

$$C_{P,\text{gas}} \simeq C_{V,\text{gas}} + Nk_B,$$

(2.8)

or we could use, rather, the molar version of the same expression,

$$C_{P,\text{gas}} \simeq C_{V,\text{gas}} + R \quad \text{(per mole of gas molecules)}.$$

(2.9)

The $C_P - C_V$ difference is therefore $\simeq 1$ in “$R$” units (see Fig. 2.4, inset).

**Liquids**

Liquids are more difficult. Unlike gases, liquids and solids are nearly incompressible, and it is almost impossible to change their temperature while holding their volumes constant. The specific heats of liquids and solids almost always imply their constant pressure heat capacity, so that, in general, for liquids and solids we can use $c_p \simeq c_v$. Also since liquids exhibit strong intermolecular interactions, additional vibrational dof turn on. We expect that these dof will enhance molar $C_P$ by at least $3/2$, in units of $R$. However this is only the beginning of a theory of liquids, and most measured $c_p$ are somewhat larger than this theory predicts, especially for liquid H$_2$O.
Solids

Solids are also complex, however they tend to be more easily analyzeable than liquids. The simplest picture of a solid is as a collection of independent oscillators, which you may imagine as $N_A$ masses on springs, each with identical frequency of oscillation but thermally agitated by interactions with the other oscillators (see Fig. 2.5).

How many degrees of freedom does an oscillator in the Einstein solid have? We have $d$ translational and $\nu$ vibrational $dof$, so the total internal energy is $U_{\text{solid}} \simeq \frac{1}{2} (d + \nu) N k_B T$. This gives

$$C_{V,\text{solid}} \equiv \frac{dU}{dT} \simeq \frac{dof}{2} N k_B.$$  \hspace{1cm} (2.10)
Figure 2.6: Molar heat capacities for all monatomic solids, in units of $R$, are approximately equal to “3” under standard conditions.

For $N = N_A$ atoms, and $dof = 6$, the molar heat capacity from Eq. 2.10 is

$$C_{V,\text{solid}} \simeq 3\, R \quad \text{(per mole of atoms)}. \quad (2.11)$$

Notice the differences between Eq. 2.11 and Eq. 2.7. First of all, the $dof$ are different! A gas has translations and rotations counted, while a solid has translations and vibrations counted. More importantly, Eq. 2.11 is per atom, not per molecule as before. The rigid bonding in solids overrides the molecular bonds and makes each atom an independent oscillator. For room temperature, this specific heat model is very good. It is called the law of Dulong and Petit and is shown in Fig. 2.6.
2.2 What is Entropy?

Finally, we wish to work on a higher level with anticipation of studying thermodynamics. We have established the state variables $P$, $V$, $T$ and $N$ that describe thermodynamic systems. And we have introduced $Q$, the heat that drives most thermodynamic systems. However, heat has the strange property that it depends on the manner in which the experiment is done. This shows up as the disparate specific heat values, $C_V$ and $C_P$. Heat is not a truly intrinsic property of any system; it is just a form of energy in motion. A better quantity, which is a state variable, is the entropy $S$:

\[ \text{Entropy is the heat per degree Kelvin; therefore } Q_m = T \Delta S. \]

Many people will argue about the true meaning of entropy, and in fact, it is beyond the scope of this course. However, a truer accounting than the statement above will have to rely on microscopic details of gases and matter that are not easily measured or verified in the lab. The concepts of state-counting and “disorder”, a widely misused term, will make frequent appearances. But for working day to day in thermodynamics, the easiest definition is that above. However, we are speaking of differential entropy and differential heat; the distinction is that the above statement is only true over small enough changes in state that the temperature is constant.

Let us try the example of a constant-volume gas. What is the infinitesimal entropy increase $dS$ as heat flows in? The heat is proportional to the infinitesimal temperature increase $dT$ via the heat capacity $C_V$, so $dS = C_V dT/T$. The final division by $T$ is the “per degree Kelvin” portion of our entropy definition. Then we integrate to find the total change in entropy (see HW).
The result integrating from initial \(i\) to final \(f\) values of temperature is:

\[
\Delta S = C_V \ln \left( \frac{T_f}{T_i} \right).
\]  
(2.12)

A similar expression gives the entropy change, heating at constant pressure:

\[
\Delta S = C_P \ln \left( \frac{T_f}{T_i} \right),
\]  
(2.13)

The entropy change for melting an ice cube comes from expressing heat as the latent heat of fusion \(L_f\) times the melted mass \(\Delta M\):

\[
\Delta S = \frac{L_f}{T_m} \Delta M,
\]  
(2.14)

with \(T_m\) the temperature of the ice, namely, \(0^\circ\) C, and for vaporization we would use boiling temperature \(T_b\) and latent heat of vaporization \(L_v\):

\[
\Delta S = \frac{L_v}{T_b} \Delta M.
\]  
(2.15)

Now we have a 5th state variable to keep track of, so we add it to our list: \(P, V, N, T, S\).

*Thermodynamics* is the study of changes in these quantities and the fact that heat is not really one of the club is very interesting. Also it is interesting that when one of these quantities *doesn’t* change, we get a new equation usually. For example, we have seen constant-\(V\), constant-\(P\), and for phase transitions constant-\(T\). Most of the time we are interested in holding \(N\) constant. So what about \(S\), is there a process that could hold it constant?
2.2.1 Adiabatic Gas Law

Imagine that a container of gas has its internal energy changed by an amount $dU$, and it (the gas) also does "$PdV$" work on its container. But imagine that this happens with no supply of external heat. Then $\Delta S = 0$! And in fact, the only way this could happen is if $dU + PdV$ equaled zero all along the steps of whatever process is happening. We call it "Adiabatic" when these circumstances hold true, and roughly speaking, the term reflects a “slowness” in the system’s behavior that keeps everything at equilibrium, eliminating the temperature differences that would produce heat.

To get to the bottom of what adiabatic processes require, we need to re-express $dU$ as our old friend, $C_VdT$. Since we said above that $dU + PdV = 0$, then $dT = -PdV/C_V$. Taking the derivative of the ideal gas law, we find $V dP + PdV = Nk_B dT = -(Nk_B/C_V)PdV$. We now pull a real sneaky trick (This is like watching a magic trick, you never take your eyes off the sleeves):

I divide my last expression by $PV$:

$$0 = \frac{dP}{P} + \frac{dV}{V} + \left( \frac{Nk_B}{C_V} \right) \frac{dV}{V}$$

$$= \frac{dP}{P} + \left( 1 + \frac{Nk_B}{C_V} \right) \frac{dV}{V}$$

$$= d(\ln P) + \frac{C_V + Nk_B}{C_V} d(\ln V)$$

$$= d(\ln P) + \frac{C_p}{C_V} d(\ln V)$$

$$= d(\ln P) + d(\ln V^{cp/c_v})$$

$$= d(\ln PV^{cp/c_v}). \quad (2.16)$$

We used every dirty calculus move we could find to derive this, including a sly appearance of Eq. 2.8 in step 4 to relate it all back to specific heats. This was a pure math exercise, mind you.
The result of these proceedings, which is actually quite simple, is called the Adiabatic Gas Law:

\[ PV^\gamma = \text{constant} \], with \( \gamma \equiv \frac{C_P}{C_V} \). \hspace{1cm} (2.17)

It sort of looks like it might be related to the ideal gas law, but this is something entirely new, and it applies at the same time as the ideal gas law, if it is applicable at all. This, e.g., means that we can write one power of \( PV \) as proportional to \( T \) and re-write Eq. 2.17 as

\[ TV^{\gamma - 1} = \text{constant}. \] \hspace{1cm} (2.18)

Notice that the requirements for adiabaticity are: no inflow or outflow of heat and no change in entropy if the process is reversible, as well. Clouds are said to cool due to adiabatic expansion as moist air rises into the atmosphere. Values for the adiabatic gas constant are shown in Fig. 2.7.
It is useful to point out that, like the $C_P - C_V$ difference, the $C_P/C_V$ ratio is well-behaved with respect to our models for the $dof$. Since we expect that $C_V \simeq \left(\frac{dof}{2}\right)R$ for one mole of gas, then $C_P \simeq (1 + \frac{dof}{2})R$ gives a difference of $C_P - C_V = R$ and a ratio of $\gamma \equiv C_P/C_V \simeq (1 + \frac{dof}{2})/\frac{dof}{2} = (2 + dof)/dof$. See if this agrees with your expectations for the values of $\gamma$ shown in Fig. 2.7. As such, $\gamma$ is a very reliable indicator of gas composition, at least in the mode of identifying monatomic versus diatomic and polyatomic species. This was in fact our main goal in examining specific heats, namely, to characterize atomic and molecular behavior from macroscopic measurements.
HOMEWORK

1. **Joule’s experiment**: A paddle stirs $1 \text{ m}^3$ of water, requiring $250 \text{ W}$ of power to drive it. If the water absorbs all of the energy, what is its temperature rise in $30 \text{ min}$?

2. **Global warming**: Estimate the energy required (a) to raise the temperature of all the world’s oceans ($\sim 10^{21} \text{ kg}$) by $1^\circ \text{ C}$ and (b) to completely boil away all of the ocean into steam, at atmospheric pressure.

3. **Thermal equilibrium**: Two solid bodies with heat capacities $C_1$, $C_2$ and temperatures $T_1$, $T_2$ are placed in contact in a cooler. Write a formula for their combined final temperature $T_f$.

4. **Ice water**: A single $1 \text{ cm}^3$ ice cube is dropped into an 8 oz. glass of water at room temperature ($68^\circ \text{ F}$). Calculate the final temperature after all of the ice has melted and thoroughly equilibrated.

5. **Ice vs. liquid N$_2$**: How many calories of heat would (a) a $1 \text{ cm}^3$ $0^\circ \text{ C}$ ice cube extract from your skin by *melting* vs. (b) a $1 \text{ cm}^3$ -196$^\circ \text{ C}$ droplet of liquid nitrogen by *boiling*. Which would hurt more?

6. **Entropy increase at constant volume**: Starting from the “Heat per degree Kelvin” definition of entropy, namely, $dS = (C_VdT)/T$, show that integration of the expression gives Eq. 2.12.

7. **Entropy change of ice water**: Go back to problem 4 and calculate the change in entropy of the ice, of the water and of the system as a whole, after the system has equilibrated.

8. **Adiabaticity**: 1 mol of He at $400 \text{ kPa}$ and $300 \text{ K}$, expands adiabatically until the pressure is $160 \text{ kPa}$. Find the final temperature.
Chapter 3

Thermodynamics of Gases

The Laws of Thermodynamics are:

1. \( dU = TdS - PdV \), for any closed system of fixed particle number \( N \).

2. \( \Delta S \geq 0 \), for all processes occurring in a system that do not expel heat.

The first law of thermodynamics is a statement of energy conservation. Any change in a system’s internal energy \( U \) must be caused either by heat, which is equivalent to the \( TdS \) term, or by work, which is the \( PdV \) term.

The second law of thermodynamics is a constraint on the direction of heat. If two systems with temperatures \( T_{\text{hot}} \) and \( T_{\text{cold}} \) are allowed to equilibrate, then the first tiny increment of heat \( \delta Q \) that flows from \( \text{hot} \) to \( \text{cold} \) will change the entropy of the \( \text{hot} \) body by \(-\delta Q/T_{\text{hot}}\) and the entropy of the \( \text{cold} \) body by \(+\delta Q/T_{\text{cold}}\). The \( \text{hot} \) body expels heat, so the second law does not apply to it. However, the second law does apply to the \( \text{cold} \) system, for which \(+\delta Q/T_{\text{cold}} \geq 0\), and it applies to the combined \( \text{hot/cold} \) system, for which

\[
\delta S = \frac{\delta Q}{T_{\text{cold}}} - \frac{\delta Q}{T_{\text{hot}}} = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}} T_{\text{cold}}} \delta Q \geq 0 ,
\]

iff \( \delta Q \) is positive; i.e., iff heat flows from \( \text{hot} \) to \( \text{cold} \). Q.E.D.
Figure 3.1: Would you recognize a 3d cow from this 2d cross-section?

The first and second laws are so generic that they can be applied to all systems with more than $N_A$ molecules (or atoms) (or particles), and they are frequently applied even to few-particle systems, e.g. protons and neutrons. The rules are simple enough that an entire calculus can be written, based on the integrals and derivatives of thermodynamic quantities: $P$, $S$, $T$, $U$, $V$, which comprise a 5-dimensional calculus!

How do we visualize 5-dimensions? We can’t, actually. We just can’t.

We can, however, draw 3d objects on a 2d chalkboard, which is in fact a projection or a slice of a 3d object, not an actual 3d object. Can we do something similar for our 5d entities? It turns out that we can, if we are allowed to hold one of our 5 quantities constant, which is like taking a 4d slice of all the possibilities. 4d objects may then be projected onto 3d surfaces, and like a myopically-examined cow (Fig. 3.1) we often project 3d onto 2d. Thermodynamics is like a cow in this respect.
3.1 Isobaric Processes: \( dP = 0 \)

As our first example, we will take the constant pressure \( P = P_0 \) slice of our 5d calculus and see what types of shapes in \( S, T, U, V \) space we discover.

The first law says \( dU = TdS - P_0dV \), and the heat term is just \( C_PdT \), as we know from the last chapter. Therefore \( dU = C_PdT - P_0dV \), or

\[
\Delta S = C_P \int_{T_i}^{T_f} \frac{dT}{T} = C_P \ln \frac{T_f}{T_i},
\]

\[
\Delta U = C_P \Delta T - P_0 \Delta V.
\]

We cannot be more specific than this without knowing the exact details of a particular system. Let us take the ideal gas law \( PV = Nk_B T \) and rewrite it

\[
PV = (C_P - C_V) T,
\]

the generalized ideal gas law. (3.1)

We have used Eq. 2.8 to eliminate the dependence on \( N \). This was the most generally true statement that we made about gases in Chapter 2, and it has no significant exceptions under standard conditions (see Fig. 2.4 inset).

Eq. 3.1 at constant pressure allows us to set \( P_0 \Delta V = (C_P - C_V) \Delta T \), which gives: \( \Delta U = C_P \Delta T - (C_P - C_V) \Delta T = C_V \Delta T \), i.e. just Eq. 2.6.

Let us summarize: \( P = P_0 \) is a constant, \( \Delta T \propto \Delta U \propto \Delta V, \Delta S \propto \Delta \ln T \).

The proportionality constants are all worked out in the above, and we are left with three classes of behaviour. In other words, \( T, U \) and \( V \) all behave similarly, while \( P \) and \( S \) behave differently. Let us plot these three behaviors using two orthogonal 2d slices through our 3d variable space, as shown in Fig. 3.2. Traditionally, these are depicted as \( P \) vs. \( V \) and \( T \) vs. \( S \), with the fifth variable \( U \) determined by its proportionality to \( T \), via \( \Delta U \equiv C_V \Delta T \).
Figure 3.2: $PV$ and $TS$ diagrams for an isobaric expansion of an ideal gas. Work done by the gas (blue) and heat inflow (orange) equal the shaded areas.

Notice that the highlighted areas under the curves in Fig. 3.2 must have units of energy. Since the one is an integral of $PdV$, it is the work done by the gas, and the other is an integral of $TdS$, so it is a heat. For our particular choice of initial $i$ and final $f$ coordinates, this gas is expanding at constant pressure, doing work on some external system in contact with it and receiving heat from an external source as well, equaling $Q_{in} = C_P \Delta T$.

An example of an isobaric system is a gas, being slowly heated or cooled, confined by a piston in a cylinder. The work done by the system in an isobaric process is simply the pressure multiplied by the change in volume.

### 3.2 Isentropic Processes: $dS = 0$

An isentropic process, it will turn out, is just an adiabatic process that is reversible. In such a case, we have constant entropy $S = S_0$. The first law, in this case, reads $dU = -PdV$, and there is no heat. Therefore, $\Delta U = -W_{by}$. We cannot say much more without specifying an equation of state.
Figure 3.3: $PV$ and $TS$ diagrams for an isentropic/adiabatic expansion. Work done by the gas (blue) is equal to the shaded area under the curve.

To proceed, we will again use Eq. 3.1 as our example. This leads directly to the adiabatic gas law, Eq. 2.17:

$$PV\gamma = \text{constant}, \text{ and } TV^{\gamma-1} = \text{constant}.$$ 

Here $\gamma \equiv C_P/C_V$, as before.

Let us summarize: $PV = (C_P - C_V)T, S = \text{constant}, \text{ and } U = - \int PdV$.

Realize that all of the “constant” terms are different and must be determined. The five independent equalities that we derived are enough to solve for all of the five variables of state. Fig. 3.3 shows what typical “isentropes” will look like in $PV$ and $TS$ state space. Notice that there is no heat expelled in an isentropic/adiabatic process!

Finally we should emphasize the difference between adiabatic and isentropic expansion. Only if one can reverse the path from $i$ to $f$ in Fig. 3.3 would the $PV$ curve be an isentrope; otherwise it is simply called an adiabat. Common examples of adiabatic expansion are the cooling of rising clouds of vapor and the compression stroke of the piston in a gasoline engine.
3.3 Isothermal Processes: $dT = 0$

In an isothermal process, the temperature remains a constant $T = T_0$. We have seen that the internal energy is estimable by equipartition, and so it is a function only of the temperature as well. This means $U = U_0$, and therefore $dU = 0$. The first law tells us, in this case, that $dU = 0 = T_0 dS - PdV$. Here, we must find that $\Delta S = Q_{in}/T_0$, so $\int PdV = Q_{in}$.

We will use the ideal gas equation of state, Eq. 3.1, yet again. Since $PV = (C_P - C_V)T_0$, we may write $P = (C_P - C_V)T_0/V$ and therefore

$$
\Delta S = \frac{Q_{in}}{T_0} = \frac{W_{bu}}{T_0} \\
= \frac{1}{V_0} \int_{V_i}^{V_f} PdV \\
= \frac{1}{V_0} \int_{V_i}^{V_f} (C_P - C_V)V_0 dV/V \\
= (C_P - C_V) \ln \frac{V_f}{V_i}.
$$

Figure 3.4: $PV$ and $TS$ diagrams for an isothermal expansion of ideal gas. Work done by the gas (blue) and heat inflow (orange) equal the shaded areas.
Figure 3.5: \( PV \) and \( TS \) diagrams for an isometric heating of an ideal gas. Heat inflow (orange) equals the shaded area under the curve.

Now we have all of the information needed to draw \( PV/TS \) diagrams for the isothermal expansion that is shown in Fig. 3.4.

Let us summarize: \[ PV \propto T \propto U = \text{constant}, \Delta S \propto \Delta \ln V, W_{\text{by}} = Q_{\text{in}}. \]

Notice that all of the input heat is converted into work!

### 3.4 Isometric Processes: \( dV = 0 \)

In an isometric process, the volume is a constant \( V = V_0 \), so no work is done by the gas. From the first law \( dU = TdS \), and \( \Delta U = Q_{\text{in}} = C_V \Delta T \). The entropy change is similar to the isobaric process, but with \( C_V \) replacing \( C_P \),

\[ \Delta S = C_V \ln \frac{T_f}{T_i}. \]

The pressure change is by the ideal gas law, \( \Delta P = (C_P - C_V) \Delta T/V_0 \), which ultimately depends on the amount of heat that is transferred into the gas. These are all the relations that are needed to make the plots in Fig. 3.5.
Figure 3.6: $PV$ and $TS$ diagrams for Carnot heat engines using ideal gas. Work done by the gas (blue) and heat inflow (orange) equal the shaded areas.

### 3.5 The Carnot Heat Engine

In the 1800s, when steam engines were designed mostly by trial and error, there was a French military engineer named Sadi Carnot who approached the theoretical problem of how an optimally efficient steam engine might operate. He supposed that a sequence of four processes, two adiabatic and two isothermal, could generate the best possible output of work for a given input of heat. His solution, called the Carnot cycle, is depicted in Fig. 3.6.

Of course we are looking at the slice and not the whole cow. Such a beast as the “Carnot Engine” does not really exist, but if it did, it might resemble the contraption shown in Fig. 3.7. Here, the four steps are constructed to lift a block, which is then removed, and the next block is lifted. The “fuel” for this engine is just heat; a hot reservoir and a cold reservoir wish to exchange heat, which this engine allows. However, the engine extracts a toll for its services. For each unit of heat transferred from hot to cold, a small amount is taken, namely, that energy which is converted into work to lift each block.
Figure 3.7: Carnot mass lifter using *hot* and *cold* reservoirs to do work.
To calculate the work $W_{by}$ done by the gas, we have to integrate the area enclosed by a closed circuit of states in the $PV$ diagram:

$$W_{by} = \int PdV$$

$$= W_{12, \text{isotherm}} + W_{23, \text{adiabat}} + W_{34, \text{isotherm}} + W_{41, \text{adiabat}}$$

$$= Q_{in} + \int_{2}^{3} PdV - Q_{out} - \int_{1}^{4} PdV$$

$$= T_{\text{hot}} \Delta S_{\text{lift}} - \Delta U_{23} + T_{\text{cold}} \Delta S_{\text{load}} - \Delta U_{41}$$

$$= \int TdS - \oint dU$$

$$= (T_{\text{hot}} - T_{\text{cold}}) \Delta S_{\text{lift}}$$

The next to the last line we could have jumped directly to from the first law; the last line exploits the perfect rectangularity of the $TS$ diagram in Fig. 3.6. The “ideal efficiency” $\eta$ is defined as the work done done per cycle, divided by the heat energy $Q_{\text{lift}} = T_{\text{hot}} \Delta S_{\text{lift}}$ input from the hot reservoir:

$$\eta \equiv \frac{W_{by}}{Q_{\text{lift}}}$$

$$= \frac{(T_{\text{hot}} - T_{\text{cold}}) \Delta S_{\text{lift}}}{T_{\text{hot}} \Delta S_{\text{lift}}}$$

$$= \frac{(T_{\text{hot}} - T_{\text{cold}})}{T_{\text{hot}}}$$

$$= 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}} \quad \text{(3.2)}$$

Eq. 3.2 is known as the Carnot efficiency. It sets an upper limit for the efficiency of heat engines that convert pure thermal energy into work. It also sets the limits for the work that is required to operate a “perfect” refrigerator. Since we used isentropic steps, this engine can be run in reverse! If you drop the mass on the lifter, it pumps heat backwards into the hot reservoir.
(imagine the back of the fridge), then the mass falls off, and the gas expands to absorb heat from the cold reservoir (the sandwiches and the sodas), which seems a strange machination but since no engine is truly reversible, it is again just a theoretical limit. These thought experiments do provide an alternate expression of the second law

**Alternate Second Law of Thermodynamics:**

*No engine can, unless powered externally, transfer heat from a body to another at a higher temperature. Therefore no refrigerator can be built whose sole effect is to reduce the temperature of one body without raising that of another.*

### 3.5.1 General Heat Engines

Below the Carnot limit, which is unattainable, other heat engines can also be thought of as drawing an amount of heat $Q_{\text{hot}}$ from a hot “source”, extracting work $W_{by}$ done by the thermodynamic system and rejecting heat $Q_{\text{cold}}$ to a “sink”. The “source” might be chemical energy stored in fuel, and the “sink” might be exhausted hot fumes from a tailpipe. From the first law, energy is conserved, and so $W_{by} = |Q_{\text{hot}}| - |Q_{\text{cold}}|$. This allows a more general definition for the thermodynamic efficiency, based on heat, $\eta \equiv W_{by}/|Q_{\text{hot}}|$, which gives

$$\eta = 1 - \frac{|Q_{\text{cold}}|}{|Q_{\text{hot}}|}, \quad (3.3)$$

which is generally valid. Notice that we have derived all of the preceding results from the first and second laws as well a from the ideal gas law in some of the final steps. But such easy math is not generally possible for the phases of matter beyond gases.
1. **Vapor Work**: To vaporize 1 g of water requires 538 cal of heat at 100° C. The resulting vapor at 1 atm occupies 1674 cm$^3$. What fraction of the heat of vaporization represents the work required to “push back” the atmosphere to make room for the vapor? \[ \]

2. **Compressor**: 1 L of oxygen at 1 atm is compressed to 500 cm$^3$. Find the new pressure if the compression is (a) isothermal, or (b) adiabatic.

3. **Molar Motor**: 1 mol of ideal gas at temperature $T_0$, pressure $P_0$ and volume $V_0$ goes through the following cycle:
   (i) halves its density isothermally,
   (ii) halves its temperature isometrically,
   (iii) halves its volume isobarically,
   (iv) returns to its initial condition via a straight line on the $PV$ diagram.
   (a) sketch the cycle on $PV$, $TV$ and $TP$ diagrams, (b) determine the work done by the gas along each leg in terms of $R$ and $T_0$.
   (recall $PV = RT$ for 1 mol.)

4. **Invent your own**: Propose and analyze a *three-legged* closed cycle that uses isothermal, isobaric, isometric or adiabatic steps. Sketch $PV$ and $TS$ diagrams and derive the work done or heat rejected each cycle.

5. **Cows**: Calculate the ideal thermal efficiency of a cow, operating as a Carnot heat engine, using the mean bovine body temperature of 40° C.

6. **Ice maker**: A 45% efficient machine is supplied 11 kW of power. How many metric tons of ice can it ideally make per day, using 57° F water?
Solids and liquids behave quite differently than gases. Unlike the case of gases where the ideal gas law prevails, the equations of state for solids or liquids can be difficult to calculate or require quite a lot of experimental data to fit. We tried to motivate a few of the typical features in Eqs. 1.11–1.12, but these capture only the broad behaviors of solids and liquids, while missing altogether other essential details. This chapter will seek to remedy that by categorizing and defining all of the properties that are common to both solids and liquids. In addition to specific heat $c_p$ and density $\rho$, there are: thermal expansion coefficients $\alpha$, bulk moduli $B$ and thermal conductivity $\kappa$ (Fig. 4.1).

The last of these will provide an opportunity to discuss the heat equation, which describes the diffusion of heat within condensed matter structures. The two important examples that we will treat are the spreading of a localized heat source and the steady-state heat current that develops across a thermal gradient, namely, a temperature difference over a distance. The heat equation is an important prototype for many other math, chemistry and physics problems, as well, so developing an intuitive understanding for its properties here will be well-rewarded in most other technical studies.
<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha_L$ (10$^{-6}$/°C)</th>
<th>$\alpha_V$ (10$^{-6}$/°C)</th>
<th>$B$ (10$^9$ Pa)</th>
<th>$\kappa$ (W/m °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>23</td>
<td>69</td>
<td>76</td>
<td>237</td>
</tr>
<tr>
<td>Beryllium</td>
<td>11.5</td>
<td>34.5</td>
<td>130</td>
<td>200</td>
</tr>
<tr>
<td>Brass</td>
<td>19</td>
<td>57</td>
<td>140</td>
<td>125</td>
</tr>
<tr>
<td>Brick</td>
<td>5.5</td>
<td>16.5</td>
<td>3</td>
<td>0.6</td>
</tr>
<tr>
<td>Concrete</td>
<td>12</td>
<td>36</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>Copper</td>
<td>17</td>
<td>51</td>
<td>140</td>
<td>401</td>
</tr>
<tr>
<td>Diamond</td>
<td>1</td>
<td>3</td>
<td>442</td>
<td>2300</td>
</tr>
<tr>
<td>Glass</td>
<td>8</td>
<td>24</td>
<td>37</td>
<td>0.8</td>
</tr>
<tr>
<td>Gold</td>
<td>14</td>
<td>42</td>
<td>180</td>
<td>318</td>
</tr>
<tr>
<td>Graphene</td>
<td>8</td>
<td>--</td>
<td>--</td>
<td>5000</td>
</tr>
<tr>
<td>Invar Alloy</td>
<td>1.2</td>
<td>3.6</td>
<td>110</td>
<td>15</td>
</tr>
<tr>
<td>Iron</td>
<td>11.1</td>
<td>33.3</td>
<td>170</td>
<td>80</td>
</tr>
<tr>
<td>Lead</td>
<td>29</td>
<td>87</td>
<td>46</td>
<td>35</td>
</tr>
<tr>
<td>Magnesium</td>
<td>26</td>
<td>78</td>
<td>45</td>
<td>156</td>
</tr>
<tr>
<td>Mercury</td>
<td>61</td>
<td>183</td>
<td>28</td>
<td>8.3</td>
</tr>
<tr>
<td>Rubber</td>
<td>77</td>
<td>231</td>
<td>1</td>
<td>0.16</td>
</tr>
<tr>
<td>Silicon</td>
<td>2.6</td>
<td>7.8</td>
<td>100</td>
<td>149</td>
</tr>
<tr>
<td>Steel</td>
<td>11</td>
<td>33</td>
<td>160</td>
<td>45</td>
</tr>
<tr>
<td>Tungsten</td>
<td>4.5</td>
<td>13.5</td>
<td>310</td>
<td>173</td>
</tr>
<tr>
<td>Wood</td>
<td>35</td>
<td>105</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>Water (liq.)</td>
<td>69</td>
<td>207</td>
<td>2.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Water (ice)</td>
<td>51</td>
<td>153</td>
<td>8.8</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Figure 4.1: Thermal and mechanical properties of condensed matter at STP.
4.1 Thermal Expansion

Heat-induced expansion has to be taken into account in many sensitive engineering and even household design problems:

- Railways and bridges need expansion joints to tolerate hot days.
- Plumbing is designed with many bends to avoid stress on the pipes.
- Metal frame windows use flexible spacers to accommodate seasonal changes.

Thermometers also exploit thermal expansion, typically by using a liquid that changes in volume due to temperature. Bi-metallic thermometers can also be made, which exploit the differing coefficients of thermal expansion for higher measurement accuracy. For solids like this, we can ignore the effects of pressure, and the volumetric thermal expansion coefficient is defined as

\[ \alpha_V \equiv \frac{1}{V} \frac{dV}{dT} \quad (4.1) \]

The fractional change in volume of a material is proportional to this coefficient and to its temperature change, so that \[ \Delta V = (\alpha_V \Delta T)V \]. There is also a linear coefficient of expansion \[ \alpha_L \equiv \frac{L^{-1}}{dL/dT} \], for which the fractional length \[ L \] of an object changes as \[ \Delta L = (\alpha_L \Delta T)L \]. For small expansions,

\[
V + \Delta V = (L + \Delta L)^3 = L^3 \left(1 + \frac{\Delta L}{L}\right)^3 \\
\approx V \left(1 + 3 \frac{\Delta L}{L}\right) = V + 3V \frac{\Delta L}{L} 
\]

Hence \[ \alpha_L \approx \frac{1}{3} \alpha_V \]. The \( \alpha_V \) are therefore thrice \( \alpha_L \), as verified in Fig. 4.1.
4.2 Isotropic Compression

The compression of a material is not technically a thermal property, although it is an important one to include for changes in volume with pressure. When we say a material is “incompressible”, e.g. to convince ourselves that \( c_p \simeq c_v \) for condensed matter, we are really saying that it has a very high resistance to compression. This quality of a material is characterized by its bulk modulus:

\[
B \equiv -V \frac{\partial P}{\partial V}.
\]  

(4.2)

Notice the minus sign. Bulk moduli are always positive, and so \( \frac{\partial P}{\partial V} \) must always be negative as was suggested by a homework problem in Chapter 1. The bulk modulus measures a material’s resistance to uniform compression under pressure. It is defined as the pressure increase needed to cause a given fractional decrease in volume, that is, the change in volume relative to its initial volume. Interestingly, its unit of measure is a unit of pressure. Generally, a (say) 5% decrease in volume of a material requires 5% of the bulk modulus \( B \) in applied additional pressure. To be even more specific, suppose that an iron sample with bulk modulus 170 GPa is to be reduced in volume by 0.5%. This requires an applied external pressure increase of \( 0.005 \times 170 \text{ GPa} = 0.85 \text{ GPa} \) (123,250 psi).

The inverse of the bulk modulus gives the material’s compressibility, so when we approximate and say that a given substance is “incompressible”, we are really saying that it has a very high bulk modulus.

There are other moduli, somewhat related to \( B \), describing deformations of a non-isotropic nature. Non-isotropy suggests some imbalance in forces. These moduli are: the shear modulus (for shearing) and the Young’s modulus (for pulling or tensile deformation) [see, e.g., mechanical engineering texts].
4.3 Thermal Conduction

Thermal conductivity $\kappa$ is a material’s ability to conduct heat [in W/(°C m)]. For a given temperature difference $\Delta T$ and an area $A$ (in m$^2$), per distance, the thermal conductivity predicts the heating rate (in W) of a material. This is expressed most concisely by an equation for the current density $J$ of heat:

$$J = -\kappa \nabla T.$$  \hfill (4.3)

Here $T(x, y, z)$ is a temperature that varies with position, and its gradient is the vector $\nabla T \equiv (\partial_x T, \partial_y T, \partial_z T)$.

Driven by temperature differences across a continuous material, the heat current density $J \equiv A^{-1}dQ/dT$ (heat per time per area) will develop and flow until all of the local temperature gradients are minimized or eliminated. This is in direct analogy with electrical current, for which $J_e = -\sigma \nabla V = \sigma \varepsilon$. Interestingly, thermal and electrical conductivities are proportional (Fig. 4.2).
Figure 4.3: Thermal currents oppose the direction of the thermal gradient.

**Linearized Gradient Approximation**

For simple applications of Eq. 4.3, we assume that the temperature varies linearly along a single direction, so the heat current is constant (Fig. 4.3):

$$ J \simeq -\kappa \frac{\Delta T}{d} . $$

(4.4)

The temperature differential of $\Delta T = T_{\text{hot}} - T_{\text{cold}}$ exists across a distance of $d$, e.g. the thickness of a wall; if one side of the wall is at a higher temperature, it transfers energy through the wall towards the cooler side. Thus the total amount of heat that flows through in a time $\Delta t$ is $\boxed{|Q| \simeq \kappa A \Delta T \Delta t / d}$.
Figure 4.4: Flux of heat current $\mathbf{J}$ through a Gaussian surface surrounding a cylindrical heat source.

Conduction Through a Pipe

Consider a pipe of length $l$. Hot steam flows inside the pipe, which has an inner radius $r_{\text{hot}}$. Heat conducts to a colder environment at outer radius $r_{\text{cold}}$. What is the rate of energy loss by heat transfer? Inside the wall of the pipe,

$$J(r) = -\kappa_{\text{pipe}} \frac{dT}{dr} .$$  \hspace{1cm} (4.5)

Since the total rate of energy loss is $\dot{Q} \equiv dQ/dt = J(r)A$, we may consider an imaginary barrier at a radial distance of $r$ from the center, for which $\dot{Q} = J(r)2\pi rl$. We combine with Eq. 4.5 to construct a differential equation:

$$dT = -\kappa_{\text{pipe}}^{-1} \dot{Q} dr/2\pi rl ,$$

which integrates to $\Delta T = -\kappa_{\text{pipe}}^{-1} \dot{Q} \Delta \ln r/2\pi l$, or

$$\dot{Q} = 2\pi l \kappa_{\text{pipe}} \frac{T_{\text{hot}} - T_{\text{cold}}}{\ln (r_{\text{cold}}/r_{\text{hot}})} .$$  \hspace{1cm} (4.6)

The dot over $Q$ makes it a heat per second [W], while $r_{\text{cold}}/r_{\text{hot}}$ are the outer/inner pipe radii. The outward flux of $\mathbf{J}$ is as shown in Fig. 4.4.
Continuity Equation for Heat

One principle that we haven’t applied in our study of heat flow is \textit{continuity}. In electricity, “continuity” is equivalent to the conservation of charge, and in thermal physics there is conservation of energy. This is best expressed by an integral expression, which you might be most comfortable thinking of as \textit{Gauss’s Law for Heat}:

\[
\dot{Q} = - \iiint_{\text{boundary}} \mathbf{J} \cdot d\mathbf{A},
\]

(4.7)

or, for a 1-d flow of heat in \(x\), \(\partial \rho_Q / \partial t = - \partial_x J_x\), where \(\rho_Q\) is “heat density”. Essentially, this formalism means that the rate of heating \(\dot{Q}\) in a region is equal to the negative of the outward “flux” of current, i.e. that the rate of change of heat density opposes the current “\textit{divergence}”, as in the case of a heat source feeding a localized zone of high temperature.

In thermal processes, the heat density \(\rho_Q\) is ill-defined. How much heat \(Q\) does a substance hold per \(\text{cm}^3\)? One estimate is to take \(c_p\) [in J/g \(^\circ\)C] times the temperature \(T\). This gives the “heat per gram”. Multiplying by the actual mass-density \(\rho\) [in g/cm\(^3\)] gives the “heat per volume”. Therefore, \[\rho_Q \approx \rho \ c_p \ T\]. This is precisely opposite to our insistence on separating heat from temperature, but if asked how much heat it takes to warm a 0 K, 1 cm\(^3\) object up to a temperature of \(T\), this is the best answer!

The 1-d heat \textit{continuity equation}, from our estimate of \(\rho_Q\), may also be concisely expressed as

\[
\rho \ c_p \frac{\partial T}{\partial t} = - \frac{\partial J_x}{\partial x}.
\]

(4.8)

This equation ensures that an \textit{increasing outflow} of heat current, constrained to a single direction, is compensated by a decrease in the local temperature.
4.4 The Heat Equation

Finally we combine Eq. 4.8 with Eq. 4.3 in 1-d, \( J_x = -\kappa \partial_x T \), to obtain the Heat Equation:

\[
\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2} ,
\]

(4.9)

where temperature is now a dynamic and spatially-varying quantity \( T(t, x) \).

\[ D \equiv \frac{\kappa}{\rho c_p} \]

is the thermal diffusion constant [in units of \( m^2/s \)]. The units of \( D \) are important and interesting; since heat doesn’t diffuse on average into any one particular direction, but rather equally outward in all directions, then the average “displacement” of heat is meaningless. However, the “displacement squared” of heat is non-zero and meaningful! The concept of mean-squared displacement roughly relates the diffusion constant \( D \) to the mean-squared displacement \( \langle x^2 \rangle \) travelled by heat in time \( \Delta t \). The RMS displacement \( x_{RMS} \equiv \sqrt{\langle x^2 \rangle} \) is estimated using \( x_{RMS} \sim \sqrt{D \Delta t} \).

Solution Between Two Hot Blocks

Two identical blocks with initial temperatures \( T_{hot} \) and \( T_{cold} \), are joined. What will their final temperature be? Will they equilibrate to the average \( T_{avg} = \frac{1}{2}(T_{hot} + T_{cold}) \), or will their temperature difference \( \Delta T = T_{hot} - T_{cold} \) be maintained? You might think that the former answer is more obvious, but actually both answers are true at separate instants, \( t = 0 \) and \( \infty \). The solution of Eq. 4.9 for this problem is the error function:

\[
T(t, x) = T_{avg} - \frac{1}{2} \Delta T \text{erf}(x/\sqrt{4Dt}) .
\]

(4.10)
What is the error function? Well it is plotted as $1 - \text{erf} (x/\sqrt{4Dt})$ in Fig. 4.5. It is a smooth, step-like function ranging from $-1$ to $1$, formally defined as

$$\text{erf} \ x \equiv \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \, dt.$$  \hfill (4.11)

and its derivative is

$$\frac{\partial \text{erf} \ x}{\partial x} = \frac{2}{\sqrt{\pi}} \left[ \int_0^{x+dx} e^{-t^2} \, dt - \int_0^x e^{-t^2} \, dt \right] dx = \frac{2}{\sqrt{\pi}} \int_x^{x+dx} e^{-t^2} \, dt dx = \frac{2}{\sqrt{\pi}} e^{-x^2}.$$  \hfill (4.12)

Eq. 4.10 is a 1-dimensional solution along the axes of two interfaced blocks, and so obviously the $y$- and $z$-components do not play a role. However, we must find the derivatives to check that it satisfies the heat equation:

$$\partial_x T(t, x) = -\frac{\Delta T}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}$$

$$\partial_t T(t, x) = \frac{\Delta T}{\sqrt{4\pi Dt}} \frac{x}{2t} e^{-x^2/4Dt}$$

$$\partial_x^2 T(t, x) = \frac{\Delta T/D}{\sqrt{4\pi Dt}} \frac{x}{2t} e^{-x^2/4Dt}.$$  \hfill (4.13)

The last line is just $D$ times the second line, and so this solution satisfies the 1-d heat equation: $\partial_t T = D \partial_x^2 T$.

What does the solution in Eq. 4.10 say? It suggests that heat equilibrates most rapidly near the temperature boundary between two adjoined blocks and that it gradually equilibrates elsewhere. Almost instantly, however, the temperature-vs-$x$ profile becomes like a straight line. This validates our linearized gradient approximation, e.g., for the heat flow through a wall. That simpler approximation suffices, in most cases, for the estimation of heat flow.
Figure 4.5: Two identical blocks with initial temperatures differing by $\Delta T$ are joined along the $x$ axis. They equilibrate to $T_{avg}$, with the temperature profile varying in time and space as given by Eq. 4.10.
Steady-State Flow Through a Rod

Imagine a long, thin rod with one end immersed in a bucket of freezing water at 0° C and another end in another bucket at 100° C. The rod’s initial temperature becomes irrelevant after a long enough time because steady-state flow will be established. In this limit, the buckets of water are exchanging heat via steady flow of current through the rod, and its temperature will vary from one end to the other. How so? The heat equation says \( \partial_t T = D \partial^2_x T \) along the rod-axis \( x \). However, it is in a constant state of replenishment of heat by the buckets, and so its temperature profile has stopped changing: \( \partial_t T = 0 \). Therefore, \( D \partial^2_x T = 0 \), as well. Can you guess the solution? The solution is, more or less, “\( x \)”.

However, we can add and multiply by constants, in which case boundary conditions are important. We will say that the cold bucket is at \( x = -d/2 \) and the hot bucket at \( x = +d/2 \), then

\[
T(x) = \frac{T_{\text{hot}} + T_{\text{cold}}}{2} + \frac{\Delta T}{d} x ,
\]

where \( \Delta T = T_{\text{hot}} - T_{\text{cold}} \). What is the heat current in the rod? If we apply Eq. 4.3, we find \( J_x = -\kappa \Delta T/d \), which is just Eq. 4.4 again. The simple solution turns out to be fairly robust. It says that heat flows right to left, i.e., heat always flows from hot to cold.
1. **Area Expansion**: Find the *area* coefficient of expansion $\alpha_A$, from $\alpha_L$.

2. **Brass Ring**: To what temperature must a 1.99 in. diameter brass *ring* at $20^\circ\text{C}$ be raised, so that a 2.00 in. sphere will just pass through it?

3. **Glycerine**: Calculate the bulk modulus of glycerine, if 1 L of the substance contracts 0.21 cm$^3$ when subjected to a pressure of 1 N/mm$^2$.

4. **Ideal Gas Properties**: From the definitions, calculate $\alpha_V$ and $B$ for an ideal gas, expressing your answer in as few terms as possible. Comment on your results.

5. **Freezing Pond**: Ice on a pond is 4 cm thick and the temperature of the water below is $0^\circ\text{C}$. At what rate does the ice become thicker when the air temperature is $-20^\circ\text{C}$?

6. **Alaskan Pipeline**: The 800 miles of 1.2 m diameter pipeline that pump oil at $44^\circ\text{C}$, through $0^\circ\text{C}$ Alaska, have a thickness of 1.3 cm. What is the heat output through these steel pipes in W?

7. **Hot Spot**: Show by *explicit differentiation* that a solution of the form

\[ T(t,x) = \frac{A}{\sqrt{t}} e^{-x^2/4Dt} + C \quad (4.15) \]

solves the heat equation Eq. 4.9, for an infinitely long solid wire, where $A$, $C$ and $D$ are constants. Set all constants equal to 1, and plot the results now from $x = -5$ to 5, at $t = 0.5$, 1 and 2. Estimate the “RMS” displacement of heat at each time. What thermal process might this solution describe?
Chapter 5

Thermal Radiation

We spoke at the beginning of this book about Planck and his fitting of Boltzmann’s constant $k_B$, as well as his own constant $h$, as a byproduct of producing a theory of “black-body” radiation. Here is the formula that Planck fit to determine these constants:

$$u_\epsilon = \frac{\epsilon^3}{\pi^2 \hbar^3 c^3} \frac{1}{e^{\epsilon/k_BT} - 1}. \quad (5.1)$$

This relation, known as Planck’s Law, gives the energy density of photons, which is actually the quantity $u_\epsilon$ [in J/m$^3$]. Eq. 5.1 says that if you build an oven, evacuate its contents and heat it up to a temperature $T$, then you will produce lots of photons. For those whose energies equal $\epsilon$ within a range $\Delta \epsilon$, the energy density of photons is $u_\epsilon \simeq (du_\epsilon/d\epsilon) \times \Delta \epsilon$.

Planck did not set out to discover photons, however. His goal was to explain the colors of light emitted by hot objects. Nonetheless, the concept of photons became fundamentally associated with Planck, as it was found that photon energies are proportional to his constant $h \simeq 1.05 \times 10^{-34}$ J·s divided by the wavelengths $\lambda$ of photons associated with light:

$$\epsilon = \frac{2\pi hc}{\lambda}. \quad (5.2)$$
5.1 Black Body Spectrum

The definition of a black body is one which is a perfect absorber and emitter of light. In the sense of color, however, no object is truly black unless it is at a temperature of 0 K. This is supported by Planck’s Law, Eq. 5.1, which is a continuous spectrum of photon energy density, as in Fig. 5.1. Ideal black-bodies have no bias toward photons with particular energies, but this is an idealization. Copper powder, e.g., burns at moderate temperatures with a greenish hue. Graphite, however, makes a very reliable black-body.

Wien’s Displacement Law for the Spectral Peak

If one constructed a perfect oven with graphite walls, its heat would appear as a visible glow at high enough temperatures: dim red at 798 K, red at 1000 K, and so on (Fig. 5.2). The basic observations shown in Fig. 5.2 give a peak in the dim, infrared/red spectrum (at low $\epsilon$), and bluer hues at high temperature (high $\epsilon$). Though hard to prove, Eq. 5.1 is maximized at

$$\epsilon_{max} \approx 2.82 \, k_B T$$

which is Wien’s displacement law.
Figure 5.2: The “perceived” color and intensity of black-bodies at increasing temperature, as determined by Eq. 5.1. Intensities are renormalized to a linear temperature scale, e.g., as hot objects viewed through a welding helmet. The hottest objects, un-renormalized, would appear simply “white hot”.
If you go back to Chapter 1, the temperature dependence of photon energies could have been guessed, since $k_B T$ is by definition the “typical” particle energy in thermal equilibrium. Essentially, the peak color we see in an oven represents its most populous photon energies, which are similar to $k_B T$.

### 5.2 Stefan-Boltzmann Law

In the laboratory, blackbody radiation is measured by the heat emanating from a small opening in a large oven. Since the entire spectrum of photon energies contribute to the energy $U$ inside an oven volume of $V$, then we have to integrate Eq. 5.1 over all photon energies to obtain:

$$
\frac{U}{V} = \frac{1}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{\epsilon^3 \, d\epsilon}{e^{\epsilon/k_B T} - 1} \approx 0.658 \times \frac{(k_B T)^4}{\hbar^3 c^3}.
\quad (5.3)
$$

This is a useful result, but a more relevant result is the heat current density $J$ emanating from the opening. As the photons come streaming out at the speed of light, we might estimate that $J \sim c \times U/V$. The units are correct, but this is still too large due to two diminishing factors:

1. Heat exits in all directions, so a perpendicular component of a photon’s speed is $c \times \cos(\theta)$. Also, the flux integral contributes a dot product factor of $\cos \theta$, as in Eq. 4.7. Averaging both terms gives $\langle \cos^2 \theta \rangle = \frac{1}{2}$.

2. Using the black-body definition of perfect emission and absorption, it is equally likely that light moves towards (absorbing) as away (emitting) from the walls of the oven, hence another diminishing factor of $\frac{1}{2}$.  
Including both factors of $1/2$, we obtain the Stefan-Boltzmann heat current:

$$J_{SB} \simeq 0.1645 \times c \times \frac{(k_B T)^4}{h^3 c^3} \simeq [460 \text{ W} \cdot \text{m}^{-2}] \times \left(\frac{T}{300 \text{ K}}\right)^4. \quad (5.4)$$

**Worked Example: Freezing in Space** – Readers who will become astronauts should pay special attention to this example. If you were placed in a perfect $0K$ vacuum and started to radiate heat as a perfect black body, how long would it take you to reach $0^\circ C$? We will approximate you as a $65 \text{ kg}$ sphere of water with a radius of $25 \text{ cm}$. Believe me, this approximation is in your favor; a sphere has minimal surface area. As you begin to “cool”, $dQ = -m c_p dT = JA dt$, and $J = \sigma_{SB} T^4$, so $dt = -m c_p \frac{dT}{(\sigma_{SB} A T^4)}$.

$\sigma_{SB}$ is the Stefan-Boltzmann constant, $5.67 \times 10^{-8} \text{Js}^{-1}\text{m}^{-2}\text{K}^{-4}$. We integrate to find $\Delta t = (mc_p/3\sigma_{SB} A)(T_f^{-3} - T_i^{-3})$. Our heat capacity is $mc_p = 272 \text{ kJ/K}$. Surface area $A$ is $0.785 \text{ m}^2$. $T_i$ and $T_f$ are $310$ and $273.15 \text{ K}$, respectively. Time to reach freezing point: *three weeks!*

Radiation is a painfully slow way to freeze to death, and actually being placed in a vacuum is a very survivable event, at least up to the few minutes you are able to survive without oxygen. The real question is, if we radiate at about $500 \text{ W/m}^3$ with surface area of $.8 \text{ m}^2$, why doesn’t our $400 \text{ W}$ output cool us at a steady rate? answer: the Stefan-Boltzmann current works in both directions. Our environment radiates back into us. Also there is an “emissivity” factor $\varepsilon$ which reduces our radiation due to not being perfectly black. This dimensionless factor of reduction and the fact that there is an inward heat current coming from our environment leads us to the net Stefan-Boltzmann heat absorption/emission rate due to thermal radiation:

$$\dot{Q}_{SB} = \varepsilon \sigma_{SB} A \Delta(T^4). \quad (5.5)$$
Figure 5.3: Emissivities of poor (left) and good (right) black-body materials.

\[ \Delta(T^4) \] is the difference \( T_{hot}^4 - T_{cold}^4 \) between the hotter and cooler regions, \( A \) is the interfacial surface area, and \( \dot{Q} \) is the heating rate [in W] of the cooler body. Some emissivities of common materials are listed in Fig. 5.3.

We see from the table of emissivities that highly reflective materials are ideal for insulation, as in the case of a vacuum sealed thermos. The exterior wall is reflective inside and will not absorb radiation across the vacuum of the thermos jacket in very large amounts. Conversely, a “good” black-body is not always black, e.g. paper which is almost as good as black asphalt.
5.3 Intensity of Thermal Radiation

If we want to measure the intensity of thermal radiation, we will use a meter with a fixed aperture area $A_a$ to collect transmitted photons from a hot object. The intensity is the flux of energy per time, and implicitly per area, so what we are really measuring is the Stefan-Boltzmann heat current $\dot{Q}_{obj}/4\pi r^2$, for a given radius $r$ of the spherical front. This is a constant if the object’s temperature is constant, but as heat propagates outwards spherically, its flux passes through a larger and larger spherical surface. Meanwhile our detector is of fixed size. How much radiated heat per second does the detector receive? Since its aperture covers only a portion of the spherical surface of the heat front, as shown in Fig. 5.4, we will measure only a proportional fraction of the total emanated energy, i.e.,

$$\dot{Q}_{detector} = \dot{Q}_{obj} \times \frac{A_a}{4\pi d^2}, \quad (5.6)$$

where $d$ is the distance from the object to the detector, as in Fig. 5.4.
Figure 5.5: Schematic of the solar system (not to scale). Pluto is no planet.

**Worked Example: Temperature of Pluto** – Pluto, our former coldest planet, can be analyzed directly from the comfort of your own desk to determine its temperature (see Fig. 5.5). Our sun’s total luminosity, its energy output per time, is \( L_S = 4 \times 10^{26} \text{ W} \). At 40 a.u. distance, \( d = 6.0 \times 10^{12} \text{ m} \), so the flux density of light at Pluto is \( F = \frac{L_S}{4\pi d^2} = 0.88 \text{ W/m}^2 \). This is the wattage of energy that strikes each square meter on Pluto. Since the planet presents a circular target of radius \( r = 1.15 \times 10^6 \text{ m} \) to the sun, its cross-section is \( \pi r^2 = 4.15 \times 10^{12} \text{ m}^2 \). This area receives \( F \times \pi r^2 = 3.66 \times 10^{12} \text{ W} \) of power. However, there is an “albedo”, or reflection coefficient of 0.5 due to Pluto’s icy surface, and it halves the received power to \( 1.83 \times 10^{12} \text{ W} \). The planet absorbs but then re-emits this radiation at some equilibrium temperature \( T \). By the Stefan-Boltzmann law for a planet surface area of \( A = 4\pi r^2 \), using Eq. 5.5, we find \( 1.83 \times 10^{12} \text{ W} \) must equal \( \sigma_{SB} T^4 \times 4\pi r^2 \) in equilibrium. Therefore the Plutorian temperature is \( T \approx 40 \text{ K} \). Google it!
HOMEWORK

1. **Simple Detector**: A radiometer receives 0.5 cal/cm²/s from an emitting black body of temperature 727°C which is 25 cm away. What is the rate of reception when the body has cooled to 527°C but has been moved to 10 cm distance?

2. **Solar Power**: From data that you can find on Wikipedia regarding the Earth, and the total solar luminosity of \( L_S = 4 \times 10^{26} \) W, calculate the average power received per square meter on Earth from the Sun during the daytime.

3. **Planetary Temperature**: From Wikipedia, again, obtain the relevant data to repeat the calculation that we did for Pluto from the notes, but instead pick *your* favorite planet (Pluto is not a planet), and estimate its equilibrium temperature \( T \) from thermal radiative processes, and use data on the planet’s albedo as well. Please compare your answer to known values obtained from any reliable source.
Appendix A
Distributions & the Boltzmann Factor

Distributions go well beyond physics, or even science, in their importance and value. Take for example calculating your grade in a class: your syllabus reads, 30% Final / 30% Lab / 40% Tests, and your final scores are 90%/100%/70%; what is your final grade $G$?

$$G = \frac{90\% \times 30\% + 100\% \times 30\% + 70\% \times 40\%}{30\% + 30\% + 40\%} = 85\%.$$ (7)

Notice that the numerator in Eq. 7 is just the denominator (summed weights) with the grades (values that are weighted) inserted multiplicatively in front.

More generally, any weighted-average over discrete data, denoted by $\langle \cdots \rangle$, may be written as a sum over indexed data times the frequency of occurrence $f$ of all the possible contributions. Let’s take an average of “$x$”:

$$\langle x \rangle = \frac{\sum_{i=1}^{N} x_i f(x_i)}{\sum_{i=1}^{N} f(x_i)},$$ (8)

where the $x_i$ are labelled by a counting index $i$, up to the $N^{th}$ data point, weighted by a distribution factor $f(x)$. In Eq. 7, the $x_i$ are the grades and the $f(x_i)$ are the weights. Another familiar example would be the center-of-mass between any two point-masses: $\langle x \rangle = (x_1 m_1 + x_2 m_2)/(m_1 + m_2)$. 

65
Now that we have mentioned center-of-mass and “point-masses”, we have opened a whole new can of worms. What if we don’t have point-masses? What if we want the center-of-mass of a meter-stick? In that case, the sums become integrals:

$$\langle x \rangle = \frac{\int_{x_{lo}}^{x_{hi}} dx \ x \ f(x)}{\int_{x_{lo}}^{x_{hi}} dx \ f(x)}.$$  \hspace{1cm} (9)

Here “hi” and “lo” label the extremals of \(x\). For a meter-stick, the likelihood of finding chunks of mass along the length of the stick is “flat”: \(f \sim 1\). Notice that I use a squiggly equals sign; the reason is that we need a proportionally correct expression here but we needn’t obtain the proportionality constant. We find \(\langle x_{\text{stick}} \rangle = \int_{0 \text{cm}}^{100 \text{cm}} dx \ x \ 1/\int_{0 \text{cm}}^{100 \text{cm}} dx \ 1 = 1/2(100\text{cm})^2/100\text{cm} = 50\text{cm}\).

What about powers of \(x\), like \(x^2\)? Easy! We just insert \(x^2\)’s instead of \(x\)’s underneath the sums and integrals of Eqs. 8 and 9:

$$\langle x^2 \rangle = \frac{\sum_{i=1}^{N} x_i^2 f(x_i)}{\sum_{i=1}^{N} f(x_i)},$$  \hspace{1cm} (10)

or

$$\langle x^2 \rangle = \frac{\int_{x_{lo}}^{x_{hi}} dx \ x^2 f(x)}{\int_{x_{lo}}^{x_{hi}} dx \ f(x)}.$$  \hspace{1cm} (11)

Of what use are these? Well now we can calculate quantities such as the “standard deviation”, i.e. the root-mean-squared deviation from average:

$$\sqrt{\langle (x - \langle x \rangle)^2 \rangle} = \sqrt{\langle x^2 \rangle - 2\langle x \rangle \langle x \rangle + \langle x \rangle^2} = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}.$$  

This is an important quantity in statistics! Notice that the averaged quantities become constants with respect to subsequent averaging above, and MOST IMPORTANTLY notice that \(\langle x^2 \rangle \neq \langle x \rangle^2\)!

Finally, I let you in on the big secret of the past two pages, relevant to physics, which is that we hardly ever care about the averaged position “\(x\)”, in heat, sound nor light; so what was the point? We want energy averages.
.1 The Boltzmann Factor

We most want to know about the average energies $\langle E \rangle$ of atoms and the distribution of these energies $f(E)$. This distribution would tell us all we need to know about the statistics of energy. But how do we calculate $f(E)$?

Consider a game where three dice are rolled and the results are added together. Every time the dice add up to a given value, we write down the results for each individual die. Different colors are used to make sure that the dice may be identified. Using Red, White and Blue, e.g., establishes a simple order in which to read the dice. Once the dice are rolled enough times:

\[
\begin{array}{ccc}
R & W & B \\
5 & 2 & 1 \\
4 & 1 & 3 \\
2 & 5 & 1 \\
6 & 1 & 1 \\
1 & 4 & 3 \\
3 & 4 & 1 \\
5 & 1 & 2 \\
5 & 2 & 1 \\
4 & 1 & 3 \\
2 & 1 & 5 \\
4 & 2 & 2 \\
2 & 5 & 1 \\
1 & 1 & 6 \\
3 & 2 & 3 \\
3 & 2 & 3 
\end{array}
\]

and so on . . .
Figure 6: A game of dice: what are the most frequent outcomes for rolling three dice so that they add to 8?

A histogram of the die results is shown in Fig. 6. It reveals exponential behavior: the die are less likely to have a high result if their summed total is constrained to a moderate value, here 8. By comparison, a single die rolled alone would never behave like this. The outcomes for a single die would either be equal in likelihood, if unconstrained, or obviously single-valued if constrained to add up to some number. However, if an “interaction” links the results on the dice, e.g. a constraint that the sum total equals 8, then a statistical effect begin to emerge, namely, exponential distribution of results.

Now, pretend that each dice is an atom and that the results are atomic energies $E$; then our constraint that the dice total equals 8 is equivalent to energy conservation, i.e. that the sum total of energies cannot change. Also the coloring scheme provides an important distinguishability between the atoms, which is not necessarily the case in a “quantum” world.
Finally, we assume that the exponential fall-off parameter from the regression in Fig. 6 is proportional to an inverse temperature $T$. Why? Because if the temperature is raised, then we should expect to roll more 6’s, and the distribution of states is skewed more toward large values. The only resulting distribution that we can get for moderate temperatures is proportional to the Boltzmann factor:

$$f_B \sim e^{-E/k_B T}.$$  \hspace{1cm} (12)

Here, the Boltzmann constant $k_B$ is the same as that fit by Planck in 1901.

Incidentally, a “temperature” can be extracted from the $0.73^x$ in Fig. 6, since that factor is the same as exp ($-x/3.2$), where 3.2 is the value of $k_B T$.

But in what sort of “dice energy units” is this temperature? If this were equivalent to room temperature, 300 K = 1/40 eV, then the units of “energy” would have to be $1/(40 \times 3.2) = 8 \text{ m eV}$. This milli-eV scale happens to be typical of small atomic displacement energies for atoms in matter. Considering that our model was a handful of dice, that’s not too shabby!

Of all the possible ways to construct games like this, it must be agreed that there was nothing special about the dice, nor their shape, nor gravity, nor anything else. So how does this model describe atoms? It turns out that atoms equilibrate by exchanging light quanta with one another, rather than by getting rolled around by the hands of some tiny gambler. These light quanta exchange energy in a conservative way so that a packet of energy lost by one atom must be picked up by another, conserving the total energy. These rules, in which the dice values add up to a constant and in which dice are distinguishable, is all that it takes to construct a model for their statistical distribution of energy, which is at the heart of Eq. 12.
.2 Integration without Integrals

Now we must apply the Boltzmann factor to an important problem, the proof of Equipartition. From Eq. 12 we will prove two examples of Equipartition, plus an exception, by using a funny math called “parameter calculus” to calculate the motional averages associated with:

- translational motion, using atomic kinetic energies \( E = \frac{1}{2} mv^2 \),
- rotational motion, using spin kinetic energies \( E = \frac{1}{2} I \omega^2 \) and
- potential energy, e.g. subject to gravity near earth with \( PE = mgz \).

Plugging these energies into the Boltzmann factor, Eq. 12, we find:

1. First, for a collection of \( \sim 10^{23} \) bouncing balls, subject to gravity and thermal agitation, what is the average height of the system?

\[
\langle z \rangle = \frac{\int_0^\infty dz \, z \, f_B(z)}{\int_0^\infty dz \, f_B(z)} = \frac{\int_0^\infty dz \, z \, e^{-mgz/k_BT}}{\int_0^\infty dz \, e^{-mgz/k_BT}}
\]

\[
= \frac{\int_0^\infty dz \, z \, e^{-\lambda z}}{\int_0^\infty dz \, e^{-\lambda z}} = \frac{-d}{d\lambda} \int_0^\infty dz \, e^{-\lambda z}
\]

\[
= -\lambda^{-2} \int_0^\infty du \, e^{-u} = \frac{\lambda^{-1}}{\int_0^\infty du \, e^{-u}} \int_0^\infty du \, \frac{e^{-u}}{\lambda}
\]

\[
= \lambda^{-1} \frac{\int_0^\infty du \, e^{-u}}{\lambda=mg/k_B T} \rightarrow k_B T/mg .
\]  

(13)

2. Next consider thermally-agitated balls inside a box. Neglecting gravity, what is the average value of \( v_x^2 \), due only to motion in \( x \), of the balls?
$$\langle v^2 \rangle = \frac{\int_{-\infty}^{+\infty} dv_x v_x^2 f_B(v_x)}{\int_{-\infty}^{+\infty} dv_x f_B(v_x)} = \frac{\int_{-\infty}^{+\infty} dv_x v_x^2 e^{-\lambda v_x^2}}{\int_{-\infty}^{+\infty} dv_x e^{-\lambda v_x^2}} = \frac{\int_{-\infty}^{+\infty} dv_x \left( -\frac{d}{d\lambda} \right) e^{-\lambda v_x^2}}{\int_{-\infty}^{+\infty} dv_x e^{-\lambda v_x^2}} = -\frac{1}{2} \lambda^{-3/2} \int_{-\infty}^{+\infty} du e^{-u^2} = \frac{1}{2} \lambda^{-1} \int_{-\infty}^{+\infty} du \frac{e^{-u^2}}{\lambda^{1/2}} \frac{1}{\lambda=1/2 m k_B T} k_B T/m . \quad (14)$$

3. Finally consider a collection of thermally-agitated tops spinning on a floor. Considering only one direction of spin, i.e. $\pm$ “up”, what is the average value of the spin-angular frequency squared, i.e. $\omega^2$?

$$\langle \omega^2 \rangle = \frac{\int_{-\infty}^{+\infty} d\omega \omega^2 f_B(\omega)}{\int_{-\infty}^{+\infty} d\omega f_B(\omega)} = \frac{\int_{-\infty}^{+\infty} d\omega \omega^2 e^{-1/2 I \omega^2/k_B T}}{\int_{-\infty}^{+\infty} d\omega e^{-1/2 I \omega^2/k_B T}} = \frac{\int_{-\infty}^{+\infty} d\omega \left( -\frac{d}{dI} \right) e^{-\lambda \omega^2}}{\int_{-\infty}^{+\infty} d\omega e^{-\lambda \omega^2}} = \frac{-\frac{d}{dI} \int_{-\infty}^{+\infty} d\omega e^{-\lambda \omega^2}}{\int_{-\infty}^{+\infty} d\omega e^{-\lambda \omega^2}} = \frac{1}{2} \lambda^{-1} \int_{-\infty}^{+\infty} du \frac{e^{-u^2}}{\lambda^{1/2}} \frac{1}{\lambda=1/2 I k_B T} k_B T/I . \quad (15)$$

The trick in each case was to re-write the top integral as some derivative, with respect to parameters, of the bottom integral. Then we factor out the difference and cancel integrals! It becomes unnecessary to evaluate integrals.
However, there’s an even deeper conclusion regarding integration without integrals; what if we re-wrote the preceding results in terms of their closely-related energy expectation values?

1. From Eq. 13, $\langle m g z \rangle = m g \langle z \rangle = m g k_B T / mg = k_B T$.

2. From Eq. 14, $\langle \frac{1}{2} m v_x^2 \rangle = \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} m k_B T / m = \frac{1}{2} k_B T$.

3. From Eq. 15, $\langle \frac{1}{2} I \omega^2 \rangle = \frac{1}{2} I \langle \omega^2 \rangle = \frac{1}{2} I k_B T / I = \frac{1}{2} k_B T$.

The answers for all energy expectation values depend only on $k_B T$. How can this be? Doesn’t the system care what its parameters are set to, e.g. the mass of the balls, the strength of gravity or the moments-of-inertia of the tops? Why don’t the details matter? This is a question for another course, and it turns out the details can matter. However, for simple, classical systems described by freshman mechanics, it happens that you can often, surprisingly, neglect all of the details of mechanics.

From Eqs. 14 and 15, cases (2) and (3), we have proven Equipartition. Each quadratic degree of freedom receives $\frac{1}{2} k_B T$ of thermal energy. The parameters could have been set to anything, and the quadratic variables could have represented any quantity that varies in magnitude from zero to $\infty$. Therefore, the energy terms that have quadratic dependence in Eq. 1.4 are replaced on-average by $\frac{1}{2} k_B T$. Meanwhile, our one example of a linear energy (gravitational potential in case 1) got a full $k_B T$, which means equipartition does not apply at all to linear potentials, but it does for springs. The methods used here are explored further in the homework of Chapter 1.