

# Classical Physics MANUSCRIPT

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August 10, 2025

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# Chapter 1

## Newtonian Mechanics

### 1 Foundation

Newton's laws of motion and universal gravitation, along with the foundations of calculus, were devised around 1687. The modern approach to these subjects differs drastically from that of the seventeenth century, particularly when it comes to *energy*. Newton was satisfied using (what we now know as) force and momentum vectors to make his conclusions. Things like potential energy and conservation of energy were popularized in later centuries by Joule, Helmholtz, and others. Noether informed us in 1918 that any differentiable symmetry of the action of a physical system leads to a conserved quantity.

In the following we use the full arsenal of the 21st century to develop Newtonian mechanics.

#### 1.1 Position, Velocity, Acceleration

Newtonian mechanics assumes a single universal reference frame in which all dynamics take place. In this scheme, it makes sense to define an origin from which all positions  $\mathbf{r}(t)$  at all times  $t$  are represented as vectors. For a pair of particles or events, we could write:

$$\begin{aligned} \text{position: } & \mathbf{r}(t) \\ \text{displacement (time): } & \mathbf{r}(t_2) - \mathbf{r}(t_1) \\ \text{displacement (space): } & \mathbf{r}_2(t) - \mathbf{r}_1(t) \\ \text{time interval: } & t_2 - t_1 = \Delta t \end{aligned}$$

The average velocity of a particle is defined as the displacement (in time) divided by the time interval. In the differential limit, this becomes the instantaneous velocity  $\mathbf{v}(t)$ :

$$\mathbf{v}(t) = \frac{d}{dt} \mathbf{r}(t)$$

The average acceleration of a particle is defined as the velocity divided by the time interval. In the differen-

tial limit, this becomes the instantaneous acceleration  $\mathbf{a}(t)$ :

$$\mathbf{a}(t) = \frac{d}{dt} \mathbf{v}(t) = \frac{d^2}{dt^2} \mathbf{r}(t)$$

For a system of  $N$  total particles, we label each particle with a subscript  $i, j$ , etc., depending on context. For instance, the  $i$ th particle has position vector  $\mathbf{r}_i$ , velocity vector  $\mathbf{v}_i$ , mass  $m_i$ , etc.

#### 1.2 Newton's Laws

The axioms of Newtonian mechanics are the famous Newton's laws, of which there are three:

1. **Law of Intertia:** An object at rest stays at rest, and an object in motion stays in motion with the same speed and in the same direction unless acted upon by an unbalanced force. This means if the total force  $\mathbf{F}$  on an object is zero, the velocity doesn't change:

$$\mathbf{F} = 0 \rightarrow \mathbf{v} = \text{constant}$$

2. **Law of Force and Acceleration:** The acceleration of an object is directly proportional to the net force  $\mathbf{F}$  acting on the object, is in the same direction as the net force, and is inversely proportional to the mass  $m$  of the object:

$$\mathbf{F} = m\mathbf{a}$$

For a system of  $N$  particles, Newton's second law reads:

$$m_i \mathbf{a}_i = \sum_{j=1}^N \mathbf{F}_{ij}$$

3. **Law of Action-Reaction:** For every action, there is an equal and opposite reaction. When one object exerts a force on another object, the second object exerts an equal force back on the first object in the opposite direction:

$$\mathbf{F}_{ij} = -\mathbf{F}_{ji}$$

### Force as Gradient

In order for Newton's second law to be of use, we need to declare several things about the force vector  $\mathbf{F}$ , more precisely the interaction between two particles  $\mathbf{F}_{ij}$ :

1. The force  $\mathbf{F}_{ij}$  depends only on the positions  $\mathbf{r}_i$ ,  $\mathbf{r}_j$ :

$$\mathbf{F}_{ij} = \mathbf{F}_{ij}(\mathbf{r}_i, \mathbf{r}_j)$$

2. The force vector is defined as the spatial derivative, i.e. the gradient of a scalar function depending only on  $\mathbf{r}_i$ ,  $\mathbf{r}_j$ :

$$\mathbf{F}_{ij} = -\frac{\partial}{\partial \mathbf{r}_i} U_{ij}(\mathbf{r}_i, \mathbf{r}_j)$$

3. The  $\mathbf{r}$ -dependence in  $U_{ij}(\mathbf{r}_i, \mathbf{r}_j)$  occurs as the magnitude of the displacement between  $\mathbf{r}_i$ ,  $\mathbf{r}_j$ :

$$U_{ij}(\mathbf{r}_i, \mathbf{r}_j) = U_{ji}(\mathbf{r}_1, \mathbf{r}_2) = U_{ij}(|\mathbf{r}_1 - \mathbf{r}_2|)$$

From the above, we reason that the strength of the interaction between two particles is, as far as space is concerned, only a function of the separation between the particles. This should mean the force vector  $\mathbf{F}_{ij}$  is equivalent to a scalar function  $f_{ij}$  multiplied by the distance  $\mathbf{r}_i - \mathbf{r}_j$  between the particles:

$$\mathbf{F}_{ij} = f_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)(\mathbf{r}_i - \mathbf{r}_j)$$

Equivalently, we have

$$\mathbf{F}_{ij} = f_{ij}(|\mathbf{r}_i - \mathbf{r}_j|) r \hat{\mathbf{r}}_{ij},$$

telling us

$$-\frac{\partial}{\partial \mathbf{r}_i} U_{ij}(r) = f_{ij}(|\mathbf{r}_i - \mathbf{r}_j|) r,$$

or

$$f_{ij}(r) = f_{ji}(r) = -\frac{1}{r} \frac{d}{dr} (U_{ij}(r)).$$

Swapping particle  $i$  with particle  $j$ , we see  $f_{ij}(r)$  remains unchanged but the unit vector  $\hat{\mathbf{r}}$  reverses sign. This constitutes a proof of Newton's third law.

In light of the interpretation of force as the gradient of a scalar function, we compile an 'updated' Newton's second law, which contains the other two laws, as:

$$m_i \mathbf{a}_i = \sum_{j=1}^N -\frac{\partial}{\partial \mathbf{r}_i} U_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)$$

### 1.3 Reference Frame

#### Galilean Invariance

Newton's laws exhibit the remarkable property that all physics remains the same when introducing a shift of coordinates

$$\mathbf{r}'_i = \mathbf{r}_i - \Delta \mathbf{r},$$

or more strongly

$$\mathbf{r}'_i = \mathbf{r}_i - \mathbf{v}_0 \Delta t,$$

where  $\mathbf{v}_0$  is a constant velocity vector. Taking a single time derivative gives an analogous statement for a shift of velocity:

$$\mathbf{v}'_i = \mathbf{v}_i - \mathbf{v}_0$$

The pattern stops before acceleration. Due to the same shift  $\Delta \mathbf{r} = \mathbf{v}_0 \Delta t$ , the acceleration remains the same:

$$\mathbf{a}'_i = \mathbf{a}_i$$

#### Problem 1

Prove the notion of Galilean invariance by evaluating:

$$m_i \mathbf{a}'_i = \sum_{j=1}^N -\frac{\partial}{\partial \mathbf{r}'_i} U_{ij}(|\mathbf{r}'_i - \mathbf{r}'_j|)$$

Hint: Simplify until all prime symbols are gone.

#### Center of Mass

The center of mass of a system of  $N$  particles denoted  $\mathbf{R}(t)$ , is defined as:

$$\mathbf{R}(t) = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2 + m_3 \mathbf{r}_3 + \cdots}{m_1 + m_2 + m_3 + \cdots}$$

The denominator is the total mass  $M$  of the system

$$M = m_1 + m_2 + m_3 + \cdots = \sum_{j=1}^N m_j,$$

and the quantity  $\mathbf{R}(t)$  is tightly expressed in sigma notation:

$$\mathbf{R}(t) = \frac{1}{M} \sum_{j=1}^N m_j \mathbf{r}_j$$

### 1.4 Momentum

For a system of  $N$  interacting particles, it should make intuitive sense that the center of mass coordinate  $\mathbf{R}(t)$  does not accelerate or rotate on its own. We establish this formally with the notation of momentum.

### Linear Momentum

Take the sum of all products  $\mathbf{p}_i = m_i \mathbf{v}_i$  in the system to yield the total linear momentum

$$\mathbf{P}(t) = \sum_{i=1}^N \mathbf{p}_i = \sum_{i=1}^N m_i \mathbf{v}_i ,$$

which is related to the center of mass via

$$\mathbf{P}(t) = M \frac{d}{dt} \mathbf{R}(t) .$$

The total linear momentum vector is a constant of motion. To prove this, take a time derivative to write

$$\begin{aligned} \frac{d}{dt} \mathbf{P}(t) &= \sum_{i=1}^N m_i \frac{d}{dt} \mathbf{v}_i \\ &= \sum_{i=1}^N \sum_{j=1}^N \mathbf{F}_{ij} , \end{aligned}$$

which seems like we did nothing.

The trick now is to swap the indices  $i \leftrightarrow j$ . The order of the sums stays the same, but the force term reverses the indices:

$$\frac{d}{dt} \mathbf{P}(t) = \sum_{i=1}^N \sum_{j=1}^N \mathbf{F}_{ji}$$

Then, use Newton's third law to restore the original  $\mathbf{F}_{ij}$  with a negative sign:

$$\frac{d}{dt} \mathbf{P}(t) = - \sum_{i=1}^N \sum_{j=1}^N \mathbf{F}_{ij}$$

At this point we're saying  $d\mathbf{P}(t)/dt$  equals the negative of itself, which can only mean  $\mathbf{P}(t)$  is constant in time.

### Angular Momentum

The total angular momentum of a system of particles is given by the sum

$$\mathbf{L}(t) = \sum_{i=1}^N \mathbf{r}_i \times m_i \mathbf{v}_i ,$$

which is also constant as we'll prove.

For the time derivative of  $\mathbf{L}(t)$ , we have

$$\frac{d}{dt} \mathbf{L}(t) = \sum_{i=1}^N \frac{d}{dt} \mathbf{r}_i \times m_i \mathbf{v}_i + \sum_{i=1}^N \mathbf{r}_i \times m_i \frac{d}{dt} \mathbf{v}_i .$$

The first term contains  $\mathbf{v}_i \times \mathbf{v}_i$ , which is zero by definition of the cross product. Simplifying what's left gives

$$\frac{d}{dt} \mathbf{L}(t) = \sum_{i=1}^N \left( \mathbf{r}_i \times \sum_{j=1}^N \mathbf{F}_{ij} \right) = \sum_{i,j} \mathbf{r}_i \times \mathbf{F}_{ij} ,$$

where substituting

$$\mathbf{F}_{ij} = f_{ij}(r) (\mathbf{r}_i - \mathbf{r}_j)$$

means

$$\frac{d}{dt} \mathbf{L}(t) = - \sum_{ij} f_{ij}(r) \mathbf{r}_i \times \mathbf{r}_j .$$

#### Problem 2

By swapping indices  $i \leftrightarrow j$  and exploiting the cross product, prove:

$$\frac{d}{dt} \mathbf{L}(t) = 0$$

### 1.5 Symmetry

Similar to Galilean invariance, the equations of Newtonian mechanics exhibit several inherent symmetries, particularly with respect to rotations in space and translations in time. In detail, this means solutions to

$$m_i \mathbf{a}_i = \sum_{j=1}^N - \frac{\partial}{\partial \mathbf{r}_i} U_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)$$

remain intact under the following changes:

1. **Coordinate Translation:** A translation is a constant shift in all position vectors such that

$$\mathbf{r}'_i = \mathbf{r}_i - \mathbf{r}_0 .$$

2. **Time Translation:** A shift of the time coordinate  $t' = t - t_0$  implies all position vectors take the form

$$\mathbf{r}'_i(t) = \mathbf{r}_i(t - t_0) .$$

3. **Time Reversal:** A reversal of the time coordinate  $t' = -t$  implies all position vectors take the form

$$\mathbf{r}'_i(t) = \mathbf{r}_i(-t) .$$

4. **Coordinate Rotation:** A rotation of all coordinates about the origin is represented by

$$(r'_i)_j = \sum_{k=1}^3 R_{jk}(r_i)_k ,$$

where  $R_{jk}$  is the rotation matrix in three dimensions.

For thoroughness we will work each of the above cases. Coordinate translations entail  $\mathbf{r}'_i = \mathbf{r}_i - \mathbf{r}_0$ , along with  $\mathbf{v}'_i = \mathbf{v}_i$  and  $\mathbf{a}'_i = \mathbf{a}_i$ . We also note that

$$\mathbf{r}'_i - \mathbf{r}'_j = \mathbf{r}_i - \mathbf{r}_j ,$$

and furthermore

$$\frac{\partial}{\partial \mathbf{r}'_i} = \frac{\partial}{\partial \mathbf{r}_i} .$$

Starting with

$$m_i \mathbf{a}'_i = \sum_{j=1}^N -\frac{\partial}{\partial \mathbf{r}'_i} U_{ij} (|\mathbf{r}'_i - \mathbf{r}'_j|)$$

and replacing all primed variables via the above yields the unprimed version. (This repeats the proof of Galilean invariance.)

For time translations, start with  $t' = t - t_0$  and take derivatives of

$$\mathbf{r}'_i(t) = \mathbf{r}_i(t - t_0)$$

to find

$$\mathbf{a}'_i(t) = \mathbf{a}_i(t - t_0) .$$

From here it suffices to build the primed version of Newton's second law from the left. Doing so, we have:

$$\begin{aligned} m_i \mathbf{a}'_i(t) &= m_i \mathbf{a}_i(t - t_0) \\ &= \sum_{j=1}^N \mathbf{F}_{ij}(\mathbf{r}_i(t - t_0), \mathbf{r}_j(t - t_0)) \\ &= \sum_{j=1}^N \mathbf{F}_{ij}(\mathbf{r}'_i(t), \mathbf{r}'_j(t)) \end{aligned}$$

### Problem 3

Show that Newton's second law is maintained under time reversal symmetry  $t \rightarrow -t$ .

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Proving that Newton's second law remains intact under coordinate rotations is a bit more technical. We first acknowledge the rotation matrix in three dimensions obeys

$$\sum_{k=1}^3 R_{ik} R_{jk} = \sum_{k=1}^3 R_{ki} R_{kj} = \delta_{ij} ,$$

which is to say the transpose is the same as the inverse

$$R^T = R^{-1} ,$$

so if  $\mathbf{r}' = R\mathbf{r}$ , then  $\mathbf{r} = R^T \mathbf{r}'$ .

We still need to see what happens to the gradient operator under coordinate rotations. For this we write using the chain rule

$$\frac{\partial}{\partial (r'_i)_j} = \sum_{k=1}^3 \frac{\partial (r_i)_k}{\partial (r'_i)_j} \frac{\partial}{\partial (r_i)_k} = \sum_{k=1}^3 R_{jk} \frac{\partial}{\partial (r_i)_k} ,$$

or

$$\frac{\partial}{\partial \mathbf{r}'_i} = R \frac{\partial}{\partial \mathbf{r}_i} .$$

The proof is now easily worked out:

$$\begin{aligned} m_i \mathbf{a}'_i &= R m_i \mathbf{a}_i = \sum_{j=1}^N -R \frac{\partial}{\partial \mathbf{r}_i} U_{ij} (|\mathbf{r}_i - \mathbf{r}_j|) \\ &= \sum_{j=1}^N -\frac{\partial}{\partial \mathbf{r}'_i} U_{ij} (|\mathbf{r}'_i - \mathbf{r}'_j|) \end{aligned}$$

## 1.6 Energy

In a system of  $N$  particles, consider the force and displacement of the  $j$ th particle as it moves from the initial position  $\mathbf{r}_i$  to the final position  $\mathbf{r}_f$ .

### Kinetic Energy

The plan is to project the force on the  $j$ th particle onto its displacement along the arc of motion, called a *work integral*:

$$W_j = m_j \int_{\mathbf{r}_i}^{\mathbf{r}_f} \mathbf{a}_j \cdot d\mathbf{r}_j$$

The work  $W$  has the same dimension as  $U(r)$ , namely energy units such as Joules.

We can evaluate the work integral without knowing the motion of the particle or the force upon it. First use the chain rule to change the integration domain from spacial to temporal:

$$W_j = m_j \int_{t_i}^{t_f} \mathbf{a}_j \cdot \mathbf{v}_j dt$$

Integrating by parts, let

$$\begin{aligned} \mathbf{U} &= m_j \mathbf{v}_j \\ d\mathbf{U} &= m_j \mathbf{a}_j dt \\ d\mathbf{V} &= \mathbf{a}_j dt \\ \mathbf{V} &= \mathbf{v}_j \end{aligned}$$

and according to the recipe,

$$W_j = (\mathbf{U} \cdot \mathbf{V}) \Big|_{t_i}^{t_f} - \int_{t_i}^{t_f} \mathbf{V} \cdot d\mathbf{U} .$$

Evaluating, we find

$$W_j = m_j (\mathbf{v}_j \cdot \mathbf{v}_j) \Big|_{t_i}^{t_f} - m_j \int_{t_i}^{t_f} \mathbf{a}_j \cdot \mathbf{v}_j ,$$

where the remaining integral is just  $W_j$  again. Thus the energy added to the  $j$ th particle throughout the motion is

$$W_j = \frac{1}{2} m_j v_j^2 \Big|_{t_i}^{t_f},$$

which we interpret as the kinetic energy, denoted  $T$ .

At a given instant in any particle's motion, the instantaneous kinetic energy is a function of the instantaneous velocity  $v_j(t)$ , precisely given by

$$T_j(v_j) = \frac{1}{2} m_j (\mathbf{v}_j \cdot \mathbf{v}_j) = \frac{1}{2} m_j v_j^2,$$

where  $m$  is the mass of the particle.

### Total Energy

For a system of  $N$  particles, the total kinetic energy is easy to write down:

$$T = \sum_{i=1}^N T_i = \frac{1}{2} \sum_{i=1}^N m_i v_i^2$$

The total potential energy involves a double sum due to the two indices on  $U_{ij}$ . For starters let's try

$$U \propto \sum_{i=1}^N \sum_{j=1}^N U_{ij},$$

but notice this double-counts the total energy. We could slip in a factor of  $1/2$  and proceed with

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N U_{ij} = \frac{1}{2} \sum_{i,j} U_{ij},$$

or more efficiently, the configuration

$$U = \sum_{j=1}^N \sum_{i=1}^j U_{ij} = \sum_{i < j} U_{ij}$$

does the same job.

The sum of the kinetic energy and the potential energy is the total energy, denoted  $E$ :

$$E = T + U = \frac{1}{2} \sum_{i=1}^N m_i v_i^2 + \sum_{i < j} U_{ij}(|\mathbf{r}_1 - \mathbf{r}_2|)$$

### Conservation of Energy

The total energy  $E$  in a system of  $N$  interacting particles is a constant. Establish this by first calculating

$$\frac{dT}{dt} = \frac{1}{2} \sum_{i=1}^N m_i (2\mathbf{v}_i \cdot \mathbf{a}_i) = \sum_{i,j} \mathbf{v}_i \cdot \mathbf{F}_{ij}.$$

To proceed we must make the right-most term into something symmetric. Impose the swap of indices  $i \leftrightarrow j$  and sum the two equations to write

$$\frac{dT}{dt} = \frac{1}{2} \sum_{i,j} (\mathbf{v}_i \cdot \mathbf{F}_{ij} + \mathbf{v}_j \cdot \mathbf{F}_{ji}).$$

Replace each force vector in terms of the gradient of the potential energy, exploiting the symmetry  $U_{ij} = U_{ji}$ :

$$\frac{dT}{dt} = \frac{-1}{2} \sum_{i,j} \left( \mathbf{v}_i \cdot \left( \frac{\partial}{\partial \mathbf{r}_i} U_{ij} \right) + \mathbf{v}_j \cdot \left( \frac{\partial}{\partial \mathbf{r}_j} U_{ij} \right) \right)$$

Notice this is exactly  $-dU/dt$  by the chain rule:

$$\frac{dU}{dt} = \frac{d}{dt} \left( \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N U_{ij} \right) = -\frac{dT}{dt}$$

Putting both results together we find

$$\frac{dE}{dt} = \frac{d}{dt} (T + U) = 0,$$

thus the total energy is conserved.

### Example: Collision of Spheres

Consider two spheres of radius  $R_{1,2}$  and mass  $m_{1,2}$ , each moving with uniform velocity  $\mathbf{v}_{1,2}$ . With this setup, the system has a total energy  $T$  (scalar) and linear momentum  $\mathbf{P}$  (vector):

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$$

$$\mathbf{P} = m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2$$

If the spheres are to make contact via an elastic collision without exchanging mass, each sphere emerges with a new velocity vector  $\mathbf{u}_{1,2}$  obeying

$$T = \frac{1}{2} m_1 u_1^2 + \frac{1}{2} m_2 u_2^2$$

$$\mathbf{P} = m_1 \mathbf{u}_1 + m_2 \mathbf{u}_2,$$

which is to say energy and momentum are conserved throughout the collision. The task is to solve for  $\mathbf{u}_1, \mathbf{u}_2$ .

To make the problem easier, we can define a momentum exchange vector  $\mathbf{q}$  such that

$$m_1 \mathbf{u}_1 = m_1 \mathbf{v}_1 - \mathbf{q}$$

$$m_2 \mathbf{u}_2 = m_2 \mathbf{v}_2 + \mathbf{q}.$$

This pair of equations can recover the answers  $\mathbf{u}_{1,2}$  from  $\mathbf{q}$ , so the whole problem becomes finding  $\mathbf{q}$ .

The two spheres exchange momentum at the point of contact, thus  $\mathbf{q}$  is normal to each sphere's surface at that point. By the same token,  $\mathbf{q}$  is parallel to the vector connecting the center of each sphere. Thus each vector on hand relates by:

$$\mathbf{q} = |q| \hat{\mathbf{n}} = |q| \left( \frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)$$

Since the positions  $\mathbf{r}_{1,2}$  are given, the direction of  $\mathbf{q}$  is already clear, and the task reduces to finding  $|q|$ .

To proceed, square each momentum exchange

equation to write

$$\begin{aligned} \frac{1}{2} m_1 u_1^2 &= \frac{1}{2} m_1 v_1^2 - \mathbf{v}_1 \cdot \mathbf{q} + \frac{q^2}{2m_1} \\ \frac{1}{2} m_2 u_2^2 &= \frac{1}{2} m_2 v_2^2 + \mathbf{v}_2 \cdot \mathbf{q} + \frac{q^2}{2m_2} \end{aligned}$$

Take the sum of these, and notice all kinetic energy terms cancel, leaving

$$0 = \mathbf{q} \cdot (\mathbf{v}_1 - \mathbf{v}_2) - q^2 \left( \frac{1}{m_1} + \frac{1}{m_2} \right) .$$

Using  $\mathbf{q} = |q| \hat{\mathbf{n}}$ , finally solve for  $|q|$ :

$$|q| = \left( \frac{2m_1 m_2}{m_1 + m_2} \right) \hat{\mathbf{n}} \cdot (\mathbf{v}_1 - \mathbf{v}_2)$$



# Chapter 2

## Central Forces

### 1 Planetary Motion

#### Early Progress

The ‘modern’ understanding of planetary motion arguably began with Johannes Kepler (1571 - 1630), whose career predates the invention of calculus and Newton’s laws of motion by decades. Already familiar with the Heliocentric model of the solar system, Kepler studied meticulously-recorded charts of night sky measurements recorded by Tycho Brahe (1546 - 1601).

Paying attention to the positions of observable planets in the night sky, Kepler astonishingly figured out that planetary orbits were elliptical in shape with the sun at a focus. This became known as Kepler’s first law, which survives to this day among two other laws written by Kepler.

Aware of Kepler’s first law, Newton proposed the existence of a law of mutual Earth-sun attraction that gives rise to elliptical planetary orbits. In the modern vector notation, he began with something like

$$\mathbf{F} = F(r) \hat{\mathbf{r}},$$

and the quest was to find whatever  $F(r)$  is.

Using the calculus of his own invention, Newton found the answer to be a unified force depending on the masses involved and the inverse square of the distance separating them. We know this as Newton’s law of universal gravitation.

The plan here is to develop the equations of planetary motion using a similar approach, at least in spirit, to Newton.

#### Shell Theorem

One assumption we’ll make early on, which happens to be *true*, and will be proven with triple integration, is *any object can be considered as a point mass located at the object’s center of mass*. For instance, if we need

to calculate the gravitational attraction between two asteroids, the shape of each does not matter. Only the center-to-center distance and the mass of each body is important.

#### Newton’s Second Law

The one-dimensional version of Newton’s second law

$$m \frac{d^2}{dt^2} x(t) = -\frac{d}{dx} U(x)$$

generalizes to more dimensions where the force and acceleration become vectors:

$$m \frac{d^2 \mathbf{r}}{dt^2} = m \frac{d\mathbf{v}}{dt} = m\mathbf{a} = \mathbf{F}$$

I avoided saying exactly how  $-dU/dx$  becomes  $\mathbf{F}$ . Note that in one dimension,

$$F = -\frac{dU}{dx}$$

is true by definition, but the three dimensional version of this requires a vector derivative operator. The exact details aren’t needed in order to proceed.

#### Newton’s Third Law

The classic phrase, *for every action, there is an equal and opposite reaction*, is Newton’s third law. It means that the force from object 1 onto object 2 is exactly opposite of the force from object 2 onto object 1. This is concisely stated via vectors:

$$\mathbf{F}_{12} = -\mathbf{F}_{21}$$

### 1.1 Two-Body Problem

Consider two bodies in space, one of mass  $m_1$  at position  $\mathbf{r}_1(t)$ , and the other of mass  $m_2$  at position

$\mathbf{r}_2(t)$ . The force imposed onto body 1 by body 2 is given by

$$m_1 \frac{d^2}{dt^2} \mathbf{r}_1(t) = m_1 \frac{d}{dt} \mathbf{v}_1(t) = \mathbf{F}_{12},$$

and the force imposed onto particle 2 by particle 1 is given by

$$m_2 \frac{d^2}{dt^2} \mathbf{r}_2(t) = m_2 \frac{d}{dt} \mathbf{v}_2(t) = \mathbf{F}_{21}.$$

This setup is called the *two-body problem*.

### Center of Mass

In the two-body system, the *center of mass* is defined as a point in space  $\mathbf{R}(t)$  such that

$$\mathbf{R}(t) = \frac{m_1 \mathbf{r}_1(t) + m_2 \mathbf{r}_2(t)}{m_1 + m_2}.$$

The time derivative of the center of mass gives a quantity called the *center of velocity*:

$$\mathbf{V}(t) = \frac{d}{dt} \mathbf{R}(t) = \frac{m_1 \mathbf{v}_1(t) + m_2 \mathbf{v}_2(t)}{m_1 + m_2}.$$

Taking the time derivative of the center of velocity gives something interesting:

$$\begin{aligned} \frac{d^2}{dt^2} \mathbf{R}(t) &= \frac{m_1 (d\mathbf{v}_1(t)/dt) + m_2 (d\mathbf{v}_2(t)/dt)}{m_1 + m_2} \\ &= \frac{\mathbf{F}_{12} + \mathbf{F}_{21}}{m_1 + m_2} = \frac{\mathbf{F}_{12} - \mathbf{F}_{12}}{m_1 + m_2} = 0 \end{aligned}$$

Evidently, the second derivative of the center of mass is precisely zero because  $\mathbf{F}_{12} = -\mathbf{F}_{21}$ , regardless of how the forces act. This means that two bodies, while free to move individually, are not accelerating anywhere as a group. Moreover, this result proves that the center of velocity  $\mathbf{V}$  is a constant  $\mathbf{V}_0$ .

### Relative Displacement

If the distance separating the two bodies is  $r$ , define a vector

$$\mathbf{r}(t) = \mathbf{r}_1(t) - \mathbf{r}_2(t)$$

with  $|\mathbf{r}| = r$ , capturing the relative displacement between the two.

Listing this with the center of mass  $\mathbf{R}(t)$ , we have a system of two equations that can be solved for  $\mathbf{r}_1(t)$ ,  $\mathbf{r}_2(t)$  separately: (We know everything is a function of  $t$  by now, so drop the extra notation.)

$$\begin{aligned} \mathbf{r}_1 &= \mathbf{R} + \frac{m_2}{m_1 + m_2} \mathbf{r} \\ \mathbf{r}_2 &= \mathbf{R} - \frac{m_1}{m_1 + m_2} \mathbf{r} \end{aligned}$$

### Reduced Mass

From the equations above, multiply through by  $m_1$ ,  $m_2$ , respectively, and take two time derivatives:

$$\begin{aligned} m_1 \frac{d^2 \mathbf{r}_1}{dt^2} &= m_1 \cancel{\frac{d^2 \mathbf{R}}{dt^2}} + \frac{m_1 m_2}{m_1 + m_2} \frac{d^2 \mathbf{r}}{dt^2} \\ m_2 \frac{d^2 \mathbf{r}_2}{dt^2} &= m_2 \cancel{\frac{d^2 \mathbf{R}}{dt^2}} - \frac{m_1 m_2}{m_1 + m_2} \frac{d^2 \mathbf{r}}{dt^2} \end{aligned}$$

These results say the same thing, as the left sides are  $\mathbf{F}_{12}$ ,  $\mathbf{F}_{21}$ , respectively, and the right sides differ by the proper negative sign.

Evidently, we have

$$\mathbf{F}_{12} = \frac{m_1 m_2}{m_1 + m_2} \frac{d^2 \mathbf{r}}{dt^2}.$$

That is, there is only one force equation to worry about, and thus one position to worry about if we work with the relative displacement vector  $\mathbf{r}$  rather than two explicit position vectors  $\mathbf{r}_{1,2}$ .

The price we pay is the mass term became a mess. This group of symbols is called the *reduced mass*:

$$m_* = \frac{m_1 m_2}{m_1 + m_2}$$

Representing the effective mass of the total system as  $m_*$ , the two-body problem is summarized in one equation:

$$\mathbf{F}_{12} = m_* \frac{d^2 \mathbf{r}}{dt^2} = m_* \mathbf{a}$$

A handy identity involving the reduced mass, somewhat reminiscent of resistors in parallel, goes as:

$$\frac{1}{m_*} = \frac{1}{m_1} + \frac{1}{m_2}$$

### Linear Momentum

The linear momentum  $\mathbf{p} = m_* \mathbf{v}$  is not constant in the two-body system. To see this, take a derivative and simplify using Newton's third law:

$$\begin{aligned} \frac{d\mathbf{p}}{dt} &= m_* \left( \frac{d\mathbf{v}_1}{dt} - \frac{d\mathbf{v}_2}{dt} \right) = m_* \left( \frac{\mathbf{F}_{12}}{m_1} - \frac{\mathbf{F}_{21}}{m_2} \right) \\ \frac{d\mathbf{p}}{dt} &= \mathbf{F}_{12} \end{aligned}$$

## 1.2 Angular Momentum

Alongside the notion of forces, we'll need to put the ideas of angular momentum to use. In particular, we can show that the angular momentum of the two-body system is constant, and find what it is.

By definition, the angular momentum  $\mathbf{L}$  of the two-body system reads

$$\mathbf{L} = m_* \mathbf{r} \times \mathbf{v},$$

where  $\mathbf{r}$  is the relative displacement vector, and  $\mathbf{v}$  is its time derivative. Now calculate the time derivative of  $\mathbf{L}$ :

$$\begin{aligned} \frac{d}{dt} \mathbf{L} &= m_* \frac{d}{dt} (\mathbf{r} \times \mathbf{v}) \\ &= m_* \left( \mathbf{v} \times \mathbf{v} + \mathbf{r} \times \frac{d\mathbf{v}}{dt} \right) \\ &= \mathbf{r} \times \mathbf{F} \end{aligned}$$

For the remaining cross product to vanish, we go back to Newton's original assumption that

$$\mathbf{F} = F(r) \hat{\mathbf{r}},$$

which means the force vector and the displacement vector are parallel. Using this, we see that the derivative of  $\mathbf{L}$  resolves to zero.

Without knowing the exact motion of the two-body system, we can still write a formula for the angular momentum. For some  $r(t)$ ,  $\theta(t)$ , we have, in polar coordinates:

$$\begin{aligned} \mathbf{r} &= r \hat{\mathbf{r}} \\ \mathbf{v} &= \frac{dr}{dt} \hat{\mathbf{r}} + r \frac{d\theta}{dt} \hat{\boldsymbol{\theta}} \end{aligned}$$

Remembering  $\hat{\mathbf{r}} \times \hat{\mathbf{r}}$  is zero, we then have

$$\mathbf{L} = m_* r^2 \frac{d\theta}{dt} (\hat{\mathbf{r}} \times \hat{\boldsymbol{\theta}}).$$

The angular momentum is a constant vector that points perpendicular to the plane of motion. We take its magnitude

$$L = m_* r^2 \frac{d\theta}{dt}$$

as a constant of motion in the two-body system.

It's easy to show that the position vector and the angular momentum vector are always perpendicular. Starting with the definition of  $\mathbf{L}$ , project  $\mathbf{r}$  into both sides:

$$\mathbf{r} \cdot \mathbf{L} = m_* \mathbf{r} \cdot (\mathbf{r} \times \mathbf{v}),$$

and then make use of the triple product:

$$\mathbf{r} \cdot \mathbf{L} = m_* \mathbf{v} \cdot (\mathbf{r} \times \mathbf{r}) = 0$$

## 1.3 Inverse-Square Acceleration

We've made it this far without knowing the magnitude gravitational force  $F(r)$ , although we have harmlessly assumed that gravity acts in a straight line. Here we will derive the proper gravitational force by using Kepler's first law as a starting point.

In detail, Kepler noticed that the orbit of any planet around the sun takes an elliptical form described by

$$r(\theta) = \frac{r_0}{1 + e \cos(\theta)},$$

where  $e$  is the *eccentricity* of the orbit, and  $r_0$  is a positive characteristic length. Notice that  $r(\theta)$  as written places the origin (the sun) at the *right* focus of the ellipse. Reverse the sign on the cosine term for the sun at the left focus.

To really get started, take the time derivative of the (constant) angular momentum of the two-body system:

$$0 = \frac{dL}{dt} = m_* r \left( 2 \frac{dr}{dt} \frac{d\theta}{dt} + r \frac{d^2\theta}{dt^2} \right)$$

Perhaps you recognize the parenthesized term as being identically the  $\hat{\boldsymbol{\theta}}$ -component of the acceleration vector in polar coordinates. In terms of  $L$ , the acceleration vector is

$$\mathbf{a} = \left( \frac{d^2r}{dt^2} - \frac{L^2}{m_*^2 r^3} \right) \hat{\mathbf{r}} + \frac{1}{m_* r} \left( \cancel{\frac{dL}{dt}} \right) \hat{\boldsymbol{\theta}}.$$

We need the polar form of the ellipse to calculate  $d^2r/dt^2$ . For this, we find, after simplifying,

$$\frac{dr}{dt} = \frac{d\theta}{dt} \frac{d}{d\theta} \left( \frac{r_0}{1 + e \cos(\theta)} \right) = \frac{L}{m_* r_0} e \sin(\theta),$$

and keep going to the second derivative:

$$\frac{d^2r}{dt^2} = \frac{L^2}{m_*^2 r^2 r_0} e \cos(\theta) = \frac{L^2}{m_*^2 r^2} \left( \frac{1}{r} - \frac{1}{r_0} \right)$$

The full acceleration vector then reads

$$\mathbf{a} = \frac{L^2}{m_*^2 r^2} \left( \frac{1}{r} - \frac{1}{r_0} \right) \hat{\mathbf{r}},$$

which simplifies nicely:

$$\mathbf{a} = \frac{-L^2}{m_*^2 r_0 r^2} \hat{\mathbf{r}}$$

This finally reveals the nature of  $F(r)$ . The  $r$ -dependence is present as  $-1/r^2$ , hence the name inverse-square acceleration.

Going back to the equations that led to the reduced mass, i.e.

$$\begin{aligned} m_1 \frac{d^2 \mathbf{r}_1}{dt^2} &= m_* \frac{d^2 \mathbf{r}}{dt^2} \\ m_2 \frac{d^2 \mathbf{r}_2}{dt^2} &= -m_* \frac{d^2 \mathbf{r}}{dt^2}, \end{aligned}$$

we can solve for the absolute acceleration of each body:

$$\begin{aligned} \mathbf{a}_1 &= \frac{m_*}{m_1} \mathbf{a} \\ \mathbf{a}_2 &= \frac{-m_*}{m_2} \mathbf{a} \end{aligned}$$

Eliminate  $\mathbf{a}$  between the two equations to recover Newton's third law:

$$m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 = 0$$

## 1.4 Universal Gravitation

Enough ground work has been done to push toward Newton's universal law of gravitation.

Recall the absolute acceleration of each body  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and replace the reduced mass  $m_*$  and acceleration  $\mathbf{a}$  with expanded forms:

$$\begin{aligned} \mathbf{a}_1 &= \left( \frac{m_2}{m_1 + m_2} \right) \frac{-L^2}{m_*^2 r_0} \frac{\hat{\mathbf{r}}}{r^2} \\ \mathbf{a}_2 &= \left( \frac{-m_1}{m_1 + m_2} \right) \frac{-L^2}{m_*^2 r_0} \frac{\hat{\mathbf{r}}}{r^2} \end{aligned}$$

Multiply each equation through by  $m_1$ ,  $m_2$ , respectively to turn accelerations into forces:

$$\begin{aligned} \mathbf{F}_{12} &= \left( \frac{m_1 m_2}{m_1 + m_2} \right) \frac{-L^2}{m_*^2 r_0} \frac{\hat{\mathbf{r}}}{r^2} \\ \mathbf{F}_{21} &= \left( \frac{-m_1 m_2}{m_1 + m_2} \right) \frac{-L^2}{m_*^2 r_0} \frac{\hat{\mathbf{r}}}{r^2} \end{aligned}$$

Newton decided to introduce a new proportionality constant  $G$ , named after 'gravity', to wrangle all of the constants inherent to the two-body, system such that

$$G = \left( \frac{1}{m_1 + m_2} \right) \frac{L^2}{m_*^2 r_0}.$$

Of course, both force equations are saying the same thing due to Newton's third law, thus we write Newton's law of universal gravitation:

$$\mathbf{F}_{12} = -G \frac{m_1 m_2}{r^2} \hat{\mathbf{r}}$$

Note that the force vector bears the 12-subscript and not the other way around. The subscript is often

omitted because the unit vector  $\hat{\mathbf{r}}$  has an implied 12-subscript that goes back to the definition of  $\mathbf{r}$ .

While this calculation was set up in the context of planetary motion, note that the gravitational force is in fact *universal*, which is to say that every pair of particles in the universe obeys the same law.

### Problem 1

Show that

$$G = \frac{L^2}{m_* m_1 m_2 r_0}.$$

## 1.5 Equations of Motion

With the law of universal gravitation on hand, we should be able to run the analysis in reverse by starting with  $\mathbf{F}_{12}$  and finishing with the shape of the ellipse, along with all other allowed possibilities.

### Acceleration

Use

$$L = m_* r^2 \frac{d\theta}{dt}$$

to eliminate  $1/r^2$  in the force vector:

$$\mathbf{F}_{12} = -G m_1 m_2 \frac{m_*}{L} \frac{d\theta}{dt} \hat{\mathbf{r}}$$

Also replace  $\mathbf{F}_{12}$  to keep simplifying

$$m_1 \mathbf{a}_1 = m_* \mathbf{a} = -G m_1 m_2 \frac{m_*}{L} \frac{d\theta}{dt} \hat{\mathbf{r}},$$

and solve for the relative acceleration:

$$\mathbf{a} = -G \frac{m_1 m_2}{L} \frac{d\theta}{dt} \hat{\mathbf{r}}$$

### Velocity

To proceed, replace the acceleration vector as the derivative of the relative velocity by  $\mathbf{a} = d\mathbf{v}/dt$ . Also replace  $\hat{\mathbf{r}}$  via  $-\hat{\mathbf{r}} = d\hat{\boldsymbol{\theta}}/d\theta$  to get

$$\frac{d\mathbf{v}}{dt} = G \frac{m_1 m_2}{L} \frac{d\theta}{dt} \frac{d\hat{\boldsymbol{\theta}}}{d\theta},$$

simplifying with the chain rule to:

$$d\mathbf{v} = G \frac{m_1 m_2}{L} d\hat{\boldsymbol{\theta}}$$

Integrate both sides of the above to get a vector equation for the velocity

$$\mathbf{v}(t) = G \frac{m_1 m_2}{L} \hat{\boldsymbol{\theta}}(t) + \mathbf{v}_0,$$

where  $\mathbf{v}_0$  is the integration constant. Letting  $\theta = 0$  correspond with the positive  $x$ -axis, it must be that  $\mathbf{v}_0 = v_0 \hat{\mathbf{y}}$ .

**Position**

To goal is get hold of a position equation  $r(\theta)$ . To get closer, calculate the full angular momentum vector:

$$\begin{aligned}\mathbf{L} &= m_* \mathbf{r} \times \mathbf{v} \\ &= m_* \mathbf{r} \times \left( G \frac{m_1 m_2}{L} \hat{\boldsymbol{\theta}} + v_0 \hat{\mathbf{y}} \right) \\ &= m_* G \frac{m_1 m_2}{L} r \left( \hat{\mathbf{r}} \times \hat{\boldsymbol{\theta}} \right) + m_* v_0 r \left( \hat{\mathbf{r}} \times \hat{\mathbf{y}} \right)\end{aligned}$$

To handle the cross products, note that

$$\begin{aligned}|\hat{\mathbf{r}} \times \hat{\boldsymbol{\theta}}| &= 1 \\ |\hat{\mathbf{r}} \times \hat{\mathbf{y}}| &= |\cos(\theta)|,\end{aligned}$$

and we can work with just magnitudes:

$$L = m_* G \frac{m_1 m_2}{L} r + m_* v_0 r \cos(\theta)$$

To simplify, use

$$G = \frac{L^2}{m_* m_1 m_2 r_0},$$

and work to isolate  $r$ , arriving at

$$r_0 = r \left( 1 + r_0 \frac{m_* v_0}{L} \cos(\theta) \right),$$

and finally get

$$r(\theta) = \frac{r_0}{1 + (m_* r_0 v_0 / L) \cos(\theta)}.$$

With  $r(\theta)$  known, the position vector is straightforwardly written:

$$\mathbf{r} = r(\theta) \hat{\mathbf{r}}$$

**Eccentricity**

Comparing the above to the general form of a conic section in polar coordinates, we pick out the eccentricity to be

$$e = \frac{m_* r_0 v_0}{L}.$$

Circular orbits arise from the special case  $v_0 = 0$ . Another special case is  $e = 1$  for a parabolic trajectory. For all  $e < 1$ , the orbit is strictly an ellipse. For  $e > 1$ , the path (also technically an orbit) is hyperbolic.

This surely nails the case shut for Kepler's first law. All results reinforce the fact that planetary orbits occur on ellipses with the sun at a focus.

The eccentricity can be expressed by a variety of combinations of terms. For a version without  $L$ , one can find

$$e = \frac{\sqrt{r_0} v_0}{\sqrt{G(m_1 + m_2)}},$$

or, if you need to get rid of  $r_0$ :

$$e = \frac{v_0 L}{G m_1 m_2}$$

In terms of the eccentricity, the equations of motion can be simplified. For the position, we simply have

$$r(\theta) = \frac{r_0}{1 + e \cos(\theta)}.$$

For the velocity and acceleration, shuffle the constants around to establish

$$\frac{G m_1 m_2}{L} = \frac{v_0}{e},$$

which is only defined for non-circular orbits. With this, we have:

$$\begin{aligned}\mathbf{v} &= v_0 \left( \frac{\hat{\boldsymbol{\theta}}}{e} + \hat{\mathbf{y}} \right) \\ \mathbf{a} &= \frac{-v_0}{e} \frac{d\theta}{dt} \hat{\mathbf{r}}\end{aligned}$$

**1.6 Runge-Lorenz Vector**

The two-body problem exhibits conservation of angular momentum via the constant vector  $\mathbf{L}$ . There is, in fact, another constant vector of motion lurking about called the *Runge-Lorenz* vector

$$\mathbf{Z} = \mathbf{v} \times \mathbf{L} - G m_1 m_2 \hat{\mathbf{r}}.$$

**Constant of Motion**

Take a time derivative to prove  $\mathbf{Z}$  is constant:

$$\begin{aligned}\frac{d}{dt} \mathbf{Z} &= \frac{d}{dt} (\mathbf{v} \times \mathbf{L}) - G m_1 m_2 \frac{d\hat{\mathbf{r}}}{dt} \\ &= \frac{d\mathbf{v}}{dt} \times \mathbf{L} + \mathbf{v} \times \frac{d\mathbf{L}}{dt} - G m_1 m_2 \frac{d\hat{\mathbf{r}}}{dt}\end{aligned}$$

Keep simplifying with

$$\frac{d\mathbf{v}}{dt} = \frac{1}{m_*} \mathbf{F} = -G \frac{m_1 m_2}{m_* r^2} \hat{\mathbf{r}},$$

and also with  $\mathbf{L} = m_* \mathbf{r} \times \mathbf{v}$ , so we have

$$\frac{d}{dt} \mathbf{Z} = G m_1 m_2 \left( -\frac{\hat{\mathbf{r}} \times (\mathbf{r} \times \mathbf{v})}{r^2} - \frac{d\hat{\mathbf{r}}}{dt} \right).$$

Replace  $\mathbf{v}$  with its polar expression and note that

$$\mathbf{r} \times \mathbf{v} = \mathbf{r} \times \left( \frac{dr}{dt} \hat{\mathbf{r}} + r \frac{d\theta}{dt} \hat{\boldsymbol{\theta}} \right) = r^2 \frac{d\theta}{dt} (\hat{\mathbf{r}} \times \hat{\boldsymbol{\theta}}),$$

and furthermore, using the BAC-CAB formula:

$$\hat{\mathbf{r}} \times (\mathbf{r} \times \mathbf{v}) = r^2 \frac{d\theta}{dt} \hat{\mathbf{r}} \times (\hat{\mathbf{r}} \times \hat{\boldsymbol{\theta}}) = -r^2 \frac{d\theta}{dt} \hat{\boldsymbol{\theta}}$$

Summarizing, we find

$$\frac{d}{dt} \mathbf{Z} = Gm_1m_2 \left( \frac{d\theta}{dt} \hat{\boldsymbol{\theta}} - \frac{d\hat{\mathbf{r}}}{dt} \right) = 0$$

as proposed.

### Perigee

With  $\mathbf{Z}$  known to be constant, we're free to evaluate it at any point along the trajectory. Choose a point  $\mathbf{r}_p = r_p \hat{\mathbf{x}}$  that has  $\mathbf{v}_p \cdot \mathbf{r}_p = 0$ , called a *perigee*:

$$\begin{aligned} \mathbf{Z} &= \mathbf{v}_p \times \mathbf{L} - Gm_1m_2 \hat{\mathbf{x}} \\ &= \mathbf{v}_p \times (m_* r_p \hat{\mathbf{x}} \times \mathbf{v}_p) - Gm_1m_2 \hat{\mathbf{x}} \\ &= (m_* r_p v_p^2 - Gm_1m_2) \hat{\mathbf{x}} \end{aligned}$$

At the perigee, the velocity  $v_p$  is momentarily equal to  $r_p d\theta/dt$ , which we'll call

$$v_p = r_p \omega_p .$$

In the same notation, the angular momentum is

$$L = m_* r_p^2 \omega_p = m_* r_p v_p ,$$

and the vector  $\mathbf{Z}$  becomes

$$\mathbf{Z} = \left( \frac{L^2}{m_* r_p} - Gm_1m_2 \right) \hat{\mathbf{x}} .$$

We can keep simplifying. Replace  $L^2$  with the expression involving  $G$ :

$$\mathbf{Z} = Gm_1m_2 \left( \frac{r_0}{r_p} - 1 \right) \hat{\mathbf{x}} .$$

The ratio  $r_0/r_p$  can be calculated by setting  $\theta = 0$  in the polar equation  $r(\theta)$  for a conic section:

$$r_p = \frac{r_0}{1 + (r_0 m_* v_0 / L)} = \frac{r_0}{1 + e}$$

Finally, the simplest form for  $\mathbf{Z}$  is:

$$\mathbf{Z} = Gm_1m_2 e \hat{\mathbf{x}}$$

What  $\mathbf{Z}$  tells us, apart from containing all information about the trajectory, is that all gravitational trajectories contain at least one perigee, defining the  $x$ -axis of the coordinate system about which the motion is symmetric.

### Apogee

The perigee is also known as the nearest distance attained between the two bodies. For an elliptical orbit or hyperbolic orbit, the perigee is given by  $\theta = 0$ :

$$r_{\text{perigee}} = \frac{r_0}{1 + e}$$

For elliptical orbits, there is also the notion of *apogee*, which is the furthest distance attained between the two bodies. Set  $\theta = \pi$  to find

$$r_{\text{apogee}} = \frac{r_0}{1 - e}$$

### Problem 2

Take derivatives of

$$r(\theta) = \frac{r_0}{1 + e \cos(\theta)}$$

to verify the locations of the perigee and apogee.

### Problem 3

Show that:

$$e = \left| \frac{r_p - r_a}{r_p + r_a} \right|$$

### Conic Trajectory

The Runge-Lorenz vector

$$\mathbf{Z} = \mathbf{v} \times \mathbf{L} - Gm_1m_2 \hat{\mathbf{r}} ,$$

together with its particular expression

$$\mathbf{Z} = Gm_1m_2 e \hat{\mathbf{x}}$$

can be used together to quickly recover the polar equation for conic sections by projecting the position vector across the equation and simplifying:

$$\begin{aligned} \mathbf{r} \cdot \mathbf{Z} &= \mathbf{r} \cdot (\mathbf{v} \times \mathbf{L}) - Gm_1m_2 \mathbf{r} \cdot \hat{\mathbf{r}} \\ rZ \cos(\theta) &= \mathbf{L} \cdot (\mathbf{r} \times \mathbf{v}) - Gm_1m_2 r \\ Gm_1m_2 r e \cos(\theta) &= \frac{L^2}{m_*} - Gm_1m_2 r \end{aligned}$$

Now solve for  $r(\theta)$  and simplify more:

$$\begin{aligned} r(\theta) &= \left( \frac{L^2}{Gm_1m_2 m_*} \right) \frac{1}{1 + e \cos(\theta)} \\ &= \frac{r_0}{1 + e \cos(\theta)} \end{aligned}$$

### Relation to Ellipse

An ellipse is classified by two perpendicular lengths we know as the semi-major and semi-minor axes, denoted  $a$ ,  $b$ , respectively. By studying the ellipse, it's straightforward to show that

$$a = \frac{r_0}{1 - e^2},$$

along with

$$b = \frac{r_0}{\sqrt{1 - e^2}},$$

so that

$$\frac{b}{a} = \sqrt{1 - e^2}$$

and

$$r_0 = \frac{b^2}{a}.$$

The  $a$ -equation can be derived by taking the difference between  $r(0)$  and  $r(\pi)$ , i.e. the distance between the perigee and apogee. This pair of points defines the distance  $2a$ .

The  $b$ -equation can be derived by finding  $r_*$ ,  $\theta_*$  that correspond to  $y = b$ , the highest point on the ellipse:

$$\begin{aligned} 0 &= \frac{d}{d\theta} (y(\theta)) = \frac{d}{d\theta} (r(\theta) \sin(\theta)) \Big|_{r_*, \theta_*} \\ &= \left( \frac{r_0 e \sin^2(\theta)}{(1 + e \cos(\theta))^2} + \frac{r_0 \cos(\theta)}{1 + e \cos(\theta)} \right) \Big|_{r_*, \theta_*} \\ &= \frac{r_*^2}{r_0} (e + \cos(\theta_*)) \end{aligned}$$

Evidently, we have

$$\cos(\theta_*) = -e.$$

Taking this with

$$\begin{aligned} b &= r_* \sin(\theta_*) \\ r_* &= \sqrt{e^2 a^2 + b^2} \end{aligned}$$

is enough to finish the job. Note that similar relationships can be drawn for hyperbolic orbits.

#### Problem 4

Show that  $\mathbf{r} \cdot \mathbf{v} = 0$  is true only at the apogee and perigee.

### Dimensionless Runge-Lorenz

The Runge-Lorenz vector can be made into a dimensionless vector  $\boldsymbol{\epsilon}$  by dividing  $Gm_1 m_2$  across the whole equation

$$\boldsymbol{\epsilon} = \frac{\mathbf{v} \times \mathbf{L}}{Gm_1 m_2} - \hat{\mathbf{r}},$$

where by the properties of  $\mathbf{Z}$ , we also know

$$\boldsymbol{\epsilon} = e \hat{\mathbf{x}}.$$

With this setup, write

$$\hat{\mathbf{r}} + e \hat{\mathbf{x}} = \frac{\mathbf{v} \times \mathbf{L}}{Gm_1 m_2},$$

and then project  $\mathbf{r}$  into each side to recover the equation of a conic section:

$$r(1 + e \cos(\theta)) = \frac{\mathbf{r} \cdot (\mathbf{v} \times \mathbf{L})}{Gm_1 m_2} = r_0$$

## 1.7 Kepler's Laws

We spent a good effort developing the nature of gravitational orbits, and it would be difficult to imagine doing this without all of the modern advantages, particularly calculus and vectors. Somehow, Kepler was able to find enough pattern in sixteenth-century astronomical data to work out three correct laws of planetary motion. The data itself was recorded by astronomer Tycho Brahe over a span of at least thirty years.

### Law of Ellipses (1609)

*The orbit of each planet is an ellipse, with the sun at a focus.*

This law we know very well by now, as did Newton. For the sun at the right focus (reverse the sign for the left focus), a planetary orbit looks like

$$r(t) = \frac{r_0}{1 + e \cos(\theta(t))},$$

where  $e$  is the eccentricity.

### Law of Equal Areas (1609)

*A line drawn between the sun and the planet sweeps out equal areas in equal times.*

This is an amazing thing to notice from looking at charts of numbers. It turns out that this law is actually stating the conservation of angular momentum, although Kepler wouldn't have known so.

To derive the law in familiar language, recall the setup for the area integral in polar coordinates, particularly

$$A = \frac{1}{2} \int_{\theta_0}^{\theta_1} r^2 d\theta.$$

In differential form, this same notion reads

$$dA = \frac{1}{2} r^2 d\theta.$$

Or, by the chain rule, we can also write

$$\frac{dA}{dt} = \frac{1}{2} r^2 \frac{d\theta}{dt} .$$

Notice, though, that  $r^2 d\theta/dt$  is also present in the angular momentum

$$L = m_* r^2 \frac{d\theta}{dt} ,$$

which can only mean

$$\frac{dA}{dt} = \frac{L}{2m_*} ,$$

thus  $dA/dt$  is constant. This is the literal mathematical statement of ‘equal areas swept in equal times’.

#### Problem 5

For a body moving on a path  $r = f(\theta)$  obeying Kepler’s second law, show that the acceleration is:

$$\mathbf{a} = \frac{L^2}{m_* r^3} \left( \frac{f''(\theta)}{f(\theta)} - 2 \left( \frac{f'(\theta)}{f(\theta)} \right)^2 - 1 \right) \hat{\mathbf{r}}$$

#### Harmonic Law (1618)

*The square of the period of a planet is directly proportional to the cube of the semi-major axis of the orbit.*

Years after his first two discoveries, Kepler discerned yet another relationship for linking the time scale of the orbit to its length scale. While Kepler only knew of the proportionality between the period  $T$  and the semi-major axis  $a$ , we can do better by finding the associated constant.

Integrate the area equation for a full period of the orbit:

$$A = \frac{1}{2} \int_0^{2\pi} r^2 d\theta = \frac{L}{2m_*} \int_0^T dt = \frac{L}{2m_*} T$$

The area is simply  $\pi ab$ , so we find

$$T = \pi ab \frac{2m_*}{L} .$$

Replace  $b$  using  $b = a\sqrt{1-e^2}$ , and eliminate  $L$  using

$$G = \frac{L^2}{m_* m_1 m_2 r_0} .$$

To deal with the  $r_0$  term, recall  $a = r_0 / (1 - e^2)$  and reason that

$$T = \frac{2\pi a^{3/2}}{\sqrt{G(m_1 + m_2)}} .$$

## 1.8 Energy Considerations

With some fine details of planetary motion finished, it’s worth pointing out that the notion of ‘energy’ was not used at all. To develop some of this now, recall that in one dimension, the force relates to the potential energy by

$$F = -\frac{d}{dx} U(x) .$$

Planetary motion, on the other hand, requires three dimensions to express the force, or two dimensions if we already know the plane of the motion. This is why the force is a vector:

$$\mathbf{F} = -\frac{Gm_1 m_2}{r^2} \hat{\mathbf{r}}$$

Notice, though, that the force is dependent on one spacial quantity, the length, which to say the force is effectively one-dimensional.

#### Gravitational Potential Energy

Since the gravitational force acts in strictly the radial direction, it stands to reason that the gravitational potential energy  $U(r)$  relates to the force by:

$$\mathbf{F}(\mathbf{r}) = -\frac{d}{dr} (U(r)) \hat{\mathbf{r}}$$

This is just like the one-dimensional Newton’s law  $F = -dU/dx$ , except the force is a vector, balanced by  $\hat{\mathbf{r}}$  on the right.

To solve for  $U(r)$ , project  $\hat{\mathbf{r}}$  into both sides of the above to get

$$\frac{Gm_1 m_2}{r^2} = \frac{d}{dr} (U(r)) ,$$

solved by:

$$U(r) = -\frac{Gm_1 m_2}{r}$$

This is the total gravitational potential energy stored between the two masses  $m_1, m_2$ .

For a more formal definition, turn Newton’s second law into a definite integral in the variable  $d\mathbf{r}$  to get

$$\int_{r_0}^{r_1} \mathbf{F}(r) \cdot d\mathbf{r} = - \int_{r_0}^{r_1} \frac{d}{dr} U(r) \hat{\mathbf{r}} \cdot d\mathbf{r} ,$$

where the integral on the right is redundant to the derivative, leaving  $U(r)$  evaluated at the endpoints:

$$\int_{r_0}^{r_1} \mathbf{F}(r) \cdot d\mathbf{r} = - (U(r_1) - U(r_0))$$

Set  $r_0$  to infinity to recover the previous form.



### Kinetic Energy

Containing two objects in total, the kinetic energy  $T$  of the two-body system is

$$T = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2.$$

What we need, however, is to express the kinetic energy in terms of the relative velocity

$$\mathbf{v} = \mathbf{v}_1 - \mathbf{v}_2.$$

Working out the algebra for this is left as an exercise, but the effort results in

$$T = \frac{1}{2}m_*v^2 + \frac{1}{2}(m_1 + m_2)V_0^2,$$

where  $V_0$  is the (constant) center of velocity of the whole system. It's harmless to set this term to zero.

### Conservation of Energy

The total energy of the two-body system is the sum of the kinetic and the potential contributions:

$$E = T + U = \frac{1}{2}m_*v^2 - \frac{Gm_1m_2}{r}$$

As it turns out, the energy of the system is constant.

To prove this, begin with Newton's second law

$$\mathbf{F} = -\frac{Gm_1m_2}{r^2}\hat{\mathbf{r}},$$

and project the velocity vector into each side:

$$\mathbf{v} \cdot \mathbf{F} = -\frac{Gm_1m_2}{r^2}(\mathbf{v} \cdot \hat{\mathbf{r}})$$

Replace  $\mathbf{F}$  on the left and  $\mathbf{v}$  on the right

$$m_*\left(\mathbf{v} \cdot \frac{d\mathbf{v}}{dt}\right) = -\frac{Gm_1m_2}{r^2}\left(\frac{dr}{dt}\hat{\mathbf{r}} + r\frac{d\theta}{dt}\hat{\boldsymbol{\theta}}\right) \cdot \hat{\mathbf{r}},$$

which simplifies to

$$\frac{1}{2}m_*\frac{d}{dt}(\mathbf{v} \cdot \mathbf{v}) = -\frac{Gm_1m_2}{r^2}\frac{dr}{dt}.$$

(Note we didn't really need the polar expression for the velocity. The  $r$ -component of the velocity is always  $dr/dt$ .) The right side can be undone with the chain rule:

$$\frac{d}{dt}\left(\frac{1}{2}m_*v^2\right) = \frac{d}{dt}\left(\frac{Gm_1m_2}{r}\right)$$

Finally, we have found

$$\frac{d}{dt}(T + U) = 0,$$

as expected.

### Apocalypse Problem

#### Problem 6

If a planet were suddenly stopped in its orbit, supposed circular, show that it would fall into the sun in a time which is  $\sqrt{2}/8$  times the period of the planet's revolution.

Answer: Begin with the total energy of the system

$$-\frac{Gm_1m_2}{a} = \frac{1}{2}m_*\left(\frac{dr}{dt}\right)^2 - \frac{Gm_1m_2}{r(t)},$$

where  $a$  is the radius of the orbit. Solve for  $dr/dt$  to get

$$\frac{dr}{dt} = \sqrt{\frac{2G(m_1 + m_2)}{a}}\sqrt{\frac{a}{r} - 1},$$

which can be separated into two equal integrals:

$$\int_a^0 \frac{dr}{\sqrt{a/r - 1}} = \sqrt{\frac{2G(m_1 + m_2)}{a}} \int_0^{t_*} dt,$$

where  $t_*$  is the answer we're after.

To solve the  $r$ -integral, choose the peculiar substitution

$$r = a \cos^2(\theta) \\ dr = -2a \cos(\theta) \sin(\theta) d\theta,$$

and the above reduces to

$$2a \int_{\pi/2}^{\pi} \cos^2(\theta) d\theta = t_* \sqrt{\frac{2G(m_1 + m_2)}{a}}.$$

The remaining  $\theta$ -integral resolves to  $\pi/4$ . Solving for  $t_*$  gives

$$t_* = \frac{\sqrt{2}}{8} \left( \frac{2\pi a^{3/2}}{\sqrt{G(m_1 + m_2)}} \right) = \frac{\sqrt{2}}{8} T,$$

as stated. This is about 0.1768 years, or just over two months, supposing there are twelve months per year on that planet.

### Inverse Cube Attraction

#### Problem 7

A particle released from rest a distance  $D$  from the origin is attracted by the force

$$F = -\frac{mk^2}{x^3}.$$

Show that the time required to fall to the origin is  $D^2/k$ . Hint:

$$v = \frac{dx}{dt} = k\sqrt{\frac{1}{x^2} - \frac{1}{D^2}}$$

## 1.9 Solid Sphere

We've taken on assumption (correctly) the shell theorem, which says a gravitational body with finite size can be treated as a point located at its center of mass.

With the shell theorem, we can calculate the gravitational force inside a uniform sphere of mass  $M$  and radius  $R$  at any distance  $r < R$  from the center. A uniform sphere has the same density throughout, which we'll call  $\lambda$ :

$$\lambda = \frac{M}{4\pi R^3/3}$$

### Force Inside Solid Sphere

At a distance  $r < R$  from the center, according to the theorem, all of the sphere's mass that is located further from the center than  $r$  can be ignored. Only the sphere's mass obeying  $r < R$  contributes to the force at distance  $r$ . This portion is called the *enclosed mass*. The enclosed mass is written  $m(r)$ , given by

$$m(r) = \lambda \frac{4}{3}\pi r^3.$$

If the test particle has mass  $m_0$ , the magnitude of the force on the test particle is

$$F(r) = -\frac{Gm_0 m(r)}{r^2} = -\frac{Gm_0 M r}{R^3}.$$

Due to the  $r^3$  factor that enters the numerator, the usual  $r^{-2}$  factor is replaced by  $r$ . The gravitational force inside a sphere grows linearly with distance until  $r = R$ .

As a vector, the force inside the solid sphere reads

$$\mathbf{F}(r) = -\frac{Gm_0 M}{R^3} \mathbf{r}.$$

### Energy Inside Solid Sphere

The gravitational potential energy inside a solid sphere is not  $U \propto -1/r$ . To find the proper answer, first define

$$\lim_{r \rightarrow \infty} U(r) = 0$$

which assumes there is no energy when infinitely far from the solid sphere, assumed centered at the origin.

Starting from infinity, let a test particle of mass  $m_0$  approach the solid sphere, eventually penetrating its surface, stopping at  $r_1$ . The energy spent during approach is broken into two integrals:

$$U(r_1) = -\int_{\infty}^R \mathbf{F}_{\text{out}} \cdot d\mathbf{r} - \int_R^{r_1} \mathbf{F}_{\text{in}} \cdot d\mathbf{r},$$

where  $\mathbf{F}_{\text{out}}$ ,  $\mathbf{F}_{\text{in}}$  are the forces felt by  $m_0$  outside and inside the sphere, respectively.

Carrying out the integrals and simplifying, one finds

$$U(r_1) = \frac{Gm_0 M}{2} \left( \frac{r_1^2}{R^3} - 3 \frac{R^2}{R^3} \right).$$

Note that the special point  $r_1 = R$  corresponds to being on the sphere's surface, and the potential energy takes a familiar form

$$U(R) = -\frac{Gm_0 M}{R}.$$

### Self Energy

The *self energy* of a solid object is the energy required to assemble the object from parts initially at infinity. Since the gravitational force is attractive, we can expect the self energy due to gravity to be negative.

Demonstrating on a uniform solid sphere of radius  $R$  and mass  $M$ , write

$$dU = -\frac{Gm}{r} dm,$$

where  $dU$  is the energy added when a particle of mass  $dm$  is added to the existing sphere of mass  $m = m(r)$ . The particle settles at radius  $r$ , and each particle does so until  $r = R$ .

Since the sphere has uniform density  $\lambda$ , we further write

$$dU = -\frac{Gm\lambda v}{r} \lambda dv,$$

where  $v = v(r)$  is the volume of the sphere. Turning the crank gives:

$$\begin{aligned} dU &= -G\lambda^2 \frac{4\pi r^3/3}{r} 4\pi r^2 dr \\ U &= -G(4\pi\lambda)^2 \frac{1}{3} \int_0^R r^4 dr \\ U &= -\frac{3}{5} \frac{GM^2}{R} \end{aligned}$$

### Variable Density

If the gravitational force inside a solid sphere is independent of position, determine the density  $\lambda(r)$  of the sphere.

While there exist more rigorous ways to solve this problem, assume the density takes the form

$$\lambda(r) = Ar^n,$$

where  $n$  is an integer and  $A$  is a unit-balancing constant. With this, all mass contained within a radius  $r < R$  is given by

$$m(r) = A \frac{4\pi}{3} r^{3+n}.$$

Then, the magnitude of the force on the particle is

$$F = -\frac{4\pi G m_0}{3} r^{1+n}.$$

If the force is to be independent of  $r$ , we must have  $n = -1$ , or  $\lambda(r) = A/r$ .

### 1.10 Gravity Near Earth

Students of classical physics find out early that the force due to gravity near Earth's surface is a vector pointing straight down

$$\mathbf{F}_g = -mg \hat{\mathbf{y}},$$

with corresponding potential energy

$$U(y) = mgy,$$

where  $y$  is the height above the surface (or a location near it), and  $g$  is the local gravitation constant:

$$g = \frac{9.8 \text{ m}}{\text{s}^2}$$

On the other hand, we just went through all the pains of showing that the gravitational force is

$$\mathbf{F}(\mathbf{r}) = -\frac{Gm_1m_2}{r^2} \hat{\mathbf{r}}$$

with potential energy

$$U(r) = -\frac{Gm_1m_2}{r}.$$

Clearly, these two pictures must be reconciled. To do so, let  $r$  be replaced by the quantity  $R + y$ , where  $R$  is a constant distance we'll take to be the radius of the Earth, and  $y$  is the effective height, approximately from sea level. What we assume throughout is that  $y \ll R$ .

Without loss of generality, we can assume all displacements are one dimensional and thus  $\hat{\mathbf{r}} = \hat{\mathbf{y}}$ . This identifies  $m_1$  for the mass of the Earth, and  $m_2$  for the mass of a test projectile.

With these restrictions, the force and energy become:

$$\begin{aligned} \mathbf{F}(y) &= -\frac{Gm_1m_2}{(R+y)^2} \hat{\mathbf{y}} \\ U(y) &= -\frac{Gm_1m_2}{(R+y)} \end{aligned}$$

Next apply binomial expansion to each denominator, particularly:

$$\begin{aligned} (R+y)^{-2} &\approx \frac{1}{R^2} - \frac{2y}{R^3} + \frac{3y^2}{R^4} - \cdots \\ (R+y)^{-1} &\approx \frac{1}{R} - \frac{y}{R^2} + \frac{y^2}{R^3} - \cdots \end{aligned}$$

To first order, the above equations become

$$\begin{aligned} \mathbf{F}(y) &\approx -\frac{Gm_1m_2}{R^2} \left(1 - \frac{2y}{R}\right) \hat{\mathbf{y}} \\ U(y) &\approx -\frac{Gm_1m_2}{R} \left(1 - \frac{y}{R}\right). \end{aligned}$$

We want the force equation to be constant, thus we see the quantity  $2y/R$  must be negligible so the effective force at the surface is

$$\mathbf{F}_g = -\frac{Gm_1m_2}{R^2} \hat{\mathbf{y}}.$$

The acceleration term is identically  $g$ :

$$g = \frac{Gm_{\text{Earth}}}{R_{\text{Earth}}^2}.$$

For the potential energy, we have

$$U(y) = U_0 + mgy,$$

where  $U_0$  is the potential energy at  $y = 0$ , often defined to be zero, and the unscripted mass  $m$  is that of a test particle (not the Earth).

Note that the first-order potential term is maintained despite  $y/R$  being a very small number. The reason for this not only to recover the form  $mgy$ , but also that the first derivative must equal a constant, which is what we asked of the force.

#### Problem 8

A person's weight is  $F_0$  at sea level. To first order in  $y$ , what is the person's weight 4km above sea level? Answer:  $F_{4\text{ km}} = F_0(1 - 2(4\text{ km})/R)$

#### Escape Velocity

In a two-body system with gravity being the only force present, suppose we imparted an initial carefully-chosen *escape velocity*  $v_e$  along the line between the bodies such that the kinetic energy goes to zero as the separation becomes infinite.

As a two-body problem, we can apply conservation of energy to write

$$\frac{1}{2}m_*v_0^2 - \frac{Gm_1m_2}{d} = \frac{1}{2}m_*v^2 - \frac{Gm_1m_2}{r} = 0,$$

where  $d$  is the initial separation between the bodies. The total energy is zero by definition.

From the energy statement, we can easily solve for the escape velocity from a starting separation  $d$ :

$$v_e = \sqrt{\frac{2Gm_1m_2}{m_*d}} = \sqrt{\frac{2G(m_1 + m_2)}{d}}$$

For the case of a small body escaping Earth, the above becomes

$$v_e \approx \sqrt{2gR_{\text{Earth}}}.$$

### Hole Through Earth

An object of mass  $m$  is dropped through a straight tube connecting two points on Earth's surface. Neglecting rotational effects and friction, what happens to the object?

Unless the hole is drilled through the center, which we will not assume, the gravitational force on the object resolves into two components - one component parallel to the tube, the other component perpendicular. The equilibrium position of the object is in the center of the tube where the parallel component of the force is zero.

Let  $\mathbf{x}$  be the parallel displacement from equilibrium, and let  $\mathbf{r}$  be the position vector from the center. The force on the object parallel to the tube is:

$$F_x = \mathbf{F}(r) \cdot \hat{\mathbf{x}} = -\frac{GMm}{R^3} (\mathbf{r} \cdot \mathbf{x}) ,$$

or

$$m \frac{d^2 x}{dt^2} = -\frac{GMm}{R^3} x = -\frac{gm}{R} x .$$

The above is the differential equation

$$\frac{d^2 x}{dt^2} = -\omega^2 x$$

for a simple harmonic oscillator solved by

$$x(t) = A \cos(\omega t + \phi) ,$$

where  $A$  is the length of the tube and  $\phi$  chooses the initial position of the object. The angular frequency  $\omega$  is given by

$$\omega = \sqrt{\frac{g}{R}} .$$

## 1.11 Energy and Orbit

### Parabolic Orbit

Suppose now that a two-body system has zero total energy

$$E = 0 .$$

but the motion is not strictly along the line connecting the two bodies. In this special case, the system is *always* at escape velocity. This does not mean the escape velocity is constant. The distance  $d$  is playing the role of  $r$  in the  $v_e$  equation.

To develop this, recall that the velocity for a parabolic orbit can be written

$$\mathbf{v} = v_0 (\hat{\boldsymbol{\theta}} + \hat{\mathbf{y}}) ,$$

which means

$$v^2 = \mathbf{v} \cdot \mathbf{v} = 2v_0^2 \frac{r_0}{r} .$$

Using the escape velocity in place of  $v$  allows us to write

$$\frac{2G(m_1 + m_2)}{r} = 2v_0^2 \frac{r_0}{r} ,$$

or

$$v_0^2 = \frac{G(m_1 + m_2)}{r_0} .$$

### Elliptical Orbit

Elliptical orbits are called *bound* orbits, and have negative total energy:

$$E < 0$$

Interestingly, if we take a parabolic orbit with  $E = 0$  and subtract a little energy from the total (by some external means), then the parabola becomes an ellipse by having the second focus come in from infinity.

We ought to be able to prove the total energy is negative for an elliptical orbit. Start with the total energy

$$E = \frac{1}{2} m_* v^2 - \frac{Gm_1 m_2}{r} ,$$

and substitute  $v^2$  using

$$\mathbf{v} = \frac{v_0}{e} (\hat{\boldsymbol{\theta}} + e \hat{\mathbf{y}}) ,$$

which excludes the case of circles. Proceeding carefully, find

$$\begin{aligned} v^2 &= \frac{v_0^2}{e^2} \left( \frac{2r_0}{r} - 1 + e^2 \right) \\ &= \frac{2Gm_1 m_2}{m_* r} - \frac{Gm_1 m_2}{m_* r_0} (1 - e^2) , \end{aligned}$$

so the kinetic term is

$$E_{\text{kin}} = \frac{Gm_1 m_2}{r} - \frac{Gm_1 m_2}{2r_0} (1 - e^2) .$$

The total energy sums the potential plus the kinetic, which happens to contain equal and opposite  $1/r$ -like terms, leaving just the constant:

$$E = \frac{-Gm_1 m_2}{2r_0} (1 - e^2) = \frac{-Gm_1 m_2}{2a} ,$$

in terms of  $v_0$ ,

$$E = -\frac{1}{2} m_* v_0^2 \left( \frac{1 - e^2}{e^2} \right) .$$

### Hyperbolic Orbit

Hyperbolic orbits are called *unbound* orbits, and have positive total energy:

$$E > 0$$

The analysis of this situation follows exactly like the elliptical case. For the total energy, you can see  $e > 1$  simply flips the sign to make

$$E = \frac{Gm_1m_2}{2a} = \frac{1}{2}m_*v_0^2 \left( \frac{e^2 - 1}{e^2} \right).$$

### Circular Orbit

For circular orbits, we need to go back to the velocity equation

$$\mathbf{v} = \frac{Gm_1m_2}{L} \hat{\boldsymbol{\theta}},$$

which has no  $v_0$ -term.

The angular momentum is

$$L = m_*R^2 \frac{d\theta}{dt} = m_*a^2 \frac{2\pi}{T},$$

where  $T$  is the period of the orbit and  $R$  is the radius. Simplifying gives

$$L = m_* \sqrt{G(m_1 + m_2)R},$$

and then the square of the velocity is:

$$v^2 = \frac{G(m_1 + m_2)}{R}$$

The time derivative of  $\mathbf{v}$  gives a familiar equation for the acceleration

$$\mathbf{a} = -\frac{Gm_1m_2}{L} \frac{d\theta}{dt} \hat{\mathbf{r}},$$

which for circular orbits simplifies to

$$\mathbf{a} = \frac{-v^2}{R} \hat{\mathbf{r}},$$

as expected for circular motion in general.

The energy of a circular orbit is

$$E = \frac{1}{2} \frac{Gm_1m_2}{R} - \frac{Gm_1m_2}{R} = \frac{-Gm_1m_2}{2R},$$

thus the kinetic energy is half the potential energy, and the total is negative.

### Eccentricity and Orbit

Begin with the Runge-Lorenz vector and replace  $\mathbf{L}$  using its definition:

$$\mathbf{Z} = \mathbf{v} \times (m_* \mathbf{r} \times \mathbf{v}) - Gm_1m_2 \hat{\mathbf{r}},$$

and square the whole equation:

$$\begin{aligned} \mathbf{Z} \cdot \mathbf{Z} &= |\mathbf{v} \times (m_* \mathbf{r} \times \mathbf{v})|^2 \\ &\quad - 2Gm_1m_2 \mathbf{v} \times (m_* \mathbf{r} \times \mathbf{v}) \cdot \hat{\mathbf{r}} + G^2m_1^2m_2^2 \end{aligned}$$

For the first term on the right, notice  $\mathbf{v}$  is perpendicular to  $\mathbf{r} \times \mathbf{v}$ , so

$$|\mathbf{v} \times (m_* \mathbf{r} \times \mathbf{v})| = m_*rv^2 |\sin(\phi)|,$$

where  $\phi$  is the angle between  $\mathbf{r}$  and  $\mathbf{v}$ .

For the second term, the scalar triple product can be rewritten

$$\mathbf{v} \times (m_* \mathbf{r} \times \mathbf{v}) \cdot \hat{\mathbf{r}} = m_* (\mathbf{r} \times \mathbf{v}) \cdot (\hat{\mathbf{r}} \times \mathbf{v}).$$

The remaining vectors are parallel and the whole quantity simplifies to

$$\mathbf{v} \times (m_* \mathbf{r} \times \mathbf{v}) \cdot \hat{\mathbf{r}} = m_*rv^2 \sin^2(\phi).$$

Rewriting  $\mathbf{Z} \cdot \mathbf{Z}$  with this in mind, we have

$$\begin{aligned} Z^2 &= (m_*rv^2)^2 \sin^2(\phi) \\ &\quad - 2Gm_1m_2m_*rv^2 \sin^2(\phi) + G^2m_1^2m_2^2, \end{aligned}$$

or

$$\frac{Z^2}{G^2m_1^2m_2^2} = 1 + \sin^2(\phi) (q^2 - 2q),$$

where

$$q = \frac{m_*rv^2}{Gm_1m_2}.$$

simplifying this further gives

$$\frac{Z^2}{G^2m_1^2m_2^2} = \cos^2(\phi) + \sin^2(\phi) (1 - q)^2$$

Finally, note that the left side is actually the square of the eccentricity, giving, after restoring  $q$ :

$$e^2 = \cos^2(\phi) + \sin^2(\phi) \left( 1 - \frac{rv^2}{G(m_1 + m_2)} \right)^2$$

This is an enlightening result. For  $\phi = 0$  the motion is purely radial and uninteresting. For all other cases, we see the combination of variables being suspiciously like to the escape velocity. Swapping this in gives

$$e^2 = \cos^2(\phi) + \sin^2(\phi) \left( 1 - \frac{2v^2}{v_e^2} \right)^2$$

We see if  $v = v_e$ , then the eccentricity is precisely one, which is consistent with what we know of parabolic orbits. Similarly we see the cases  $v < v_e$  and  $v > v_e$  give  $e < 1$  and  $e > 1$  respectively, which is the signature of elliptic and hyperbolic orbits. A circular orbit has  $\phi = \pi/2$ .

### 1.12 Shell Theorem

Newton's law of gravitation tells us that every particle in the universe is trying to pull every other particle toward itself with a force proportional to the masses involved and inversely proportional to the square of the separation, and this is duly used to calculate the force onto planets, moons, satellites, and so on.

Using triple integration and spherical coordinates, something Newton didn't have, we finally address an assumption made early in gravitational analysis, namely *why* we're allowed to represent voluminous objects as single points located at the center of mass. This is called the shell theorem, and entails two important proofs.

#### Outside a Sphere

Consider a solid sphere of radius  $R$ , total mass  $M$ , and uniform density  $\lambda$ . Also let there be a test particle of mass  $m$  somewhere in space. Without loss of generality, place the test particle on the  $z$ -axis at the point  $\mathbf{D} = D \hat{\mathbf{z}}$ . The length  $D$  is the distance from the test particle to the center of the sphere.

In order to 'properly' calculate the gravitational attraction between the test mass and the sphere, a volume integral over the entire sphere must be calculated. Choose any element of volume  $dV$  inside the sphere at location  $\mathbf{r}$ , which is located distance  $r$  from the center, at an angle  $\theta$  from the  $z$ -axis.

Let vector  $\mathbf{q}$  denote the line connecting  $\mathbf{D}$  to  $\mathbf{r}$  such that

$$\mathbf{r} + \mathbf{q} = D \hat{\mathbf{z}},$$

and also let  $\alpha$  be the angle between  $\hat{\mathbf{z}}$  and  $\hat{\mathbf{q}}$ . From the law of cosines, we can say:

$$\begin{aligned} q^2 &= r^2 + D^2 - 2rD \cos(\theta) \\ r^2 &= q^2 + D^2 - 2qD \cos(\alpha) \end{aligned}$$

The total force on the test particle is the vector  $\mathbf{F}$ . However, due to the  $\phi$ -symmetry of this picture, only the  $z$ -component of the force will have a net effect on the particle. All  $xy$ -components cancel equally and oppositely:

$$\mathbf{F} = \int_{\mathcal{D}} d\mathbf{F} \cdot \hat{\mathbf{z}} = \int \int \int_{\text{volume}} dF \cos(\alpha)$$

The differential force is

$$dF = \frac{-Gm}{q^2} dm,$$

where  $dm$  is the mass of the differential volume element influencing the test particle. The mass term

can be replaced using the density

$$\frac{dm}{dV} = \frac{M}{4\pi R^3/3} = \lambda,$$

where it is appropriate to replace  $dV$  with the volume element in spherical coordinates.

The force integral now is

$$F = -Gm\lambda \int_0^{2\pi} \int_0^\pi \int_0^R \frac{\cos(\alpha)}{q^2} r^2 \sin(\theta) dr d\theta d\phi,$$

which, after substituting and simplifying a bit, becomes:

$$F = -Gm\lambda \frac{2\pi}{D^2} \int_0^\pi \int_0^R \left( \frac{1}{q} + \frac{D^2 - r^2}{q^3} \right) r^2 \sin(\theta) dr d\theta$$

Perform implicit differentiation on the  $q^2$  equation to find, remembering  $r$  and  $\theta$  are independent,

$$q dq = r D \sin(\theta) d\theta,$$

and rewrite the integral with the intent of integrating over  $r$  last. Make sure you know why the limits are now changed:

$$F = -Gm\lambda \frac{\pi}{D^2} \int_0^R \int_{(D-r)}^{(D+r)} \left( 1 + \frac{D^2 - r^2}{q^2} \right) r dq dr$$

The whole  $q$ -integral treats  $r$  as a constant and resolves to  $4r$ , so

$$F = -Gm\lambda \frac{\pi}{D^2} \int_0^R 4r^2 dr,$$

and the  $r$ -integral is elementary. Simplifying everything gives

$$F = -Gm \left( \frac{3M}{4\pi R^3} \right) \frac{\pi}{D^2} \frac{4}{3} R^3 = \frac{-GMm}{D^2}.$$

Conveniently, the force acts as if *all* of its mass were concentrated at the center. This result is also true in general, where the notion of 'center' means center of mass, not necessarily the center of the volume.

### Inside a Shell

Another interesting question that arises in the course of studying gravity is, what does it feel like inside a hollow uniform shell? To pursue this question, suppose we have a thin spherical shell of radius  $R$  and thickness  $2a$  that is much less than  $R$ , and the test particle is inside anywhere within the shell.

This setup borrows all of the geometry from the previous setup, except this time we have  $D < R$ , which is the important part. Setting up the same integral and doing the same simplifications, we can jump to

$$F = -Gm\lambda \frac{\pi}{D^2} \int_{R-a}^{R+a} \int_{(r-D)}^{(D+r)} \left(1 + \frac{D^2 - r^2}{q^2}\right) r \, dq \, dr .$$

Most notably, the lower integration in the  $q$ -integral is swapped to accommodate  $D < R$ . This causes the  $q$ -integral to resolve to zero, and we find

$$F = 0$$

inside the shell.

## 2 Central Potential

The whole apparatus for studying planetary motion can be grown from the gravitational potential energy

$$U(r) = -\frac{Gm_1m_2}{r}$$

of a two-body system. The plan now is to develop the theory while assuming as little as possible about  $U(r)$ .

### Two-Body Analysis

As a two-body system, we still deal with the center of mass

$$\mathbf{R}(t) = \frac{m_1\mathbf{r}_1(t) + m_2\mathbf{r}_2(t)}{m_1 + m_2} ,$$

whose time derivative is the center of velocity  $\mathbf{V}(t)$ . Two time derivatives of  $\mathbf{R}(t)$  yields the center of acceleration, which is always zero by Newton's third law:

$$\frac{d^2}{dt^2} \mathbf{R}(t) = 0$$

In terms of  $\mathbf{R}$ , the absolute position of each body is

$$\begin{aligned} \mathbf{r}_1 &= \mathbf{R} + \frac{m_2}{m_1 + m_2} \mathbf{r} \\ \mathbf{r}_2 &= \mathbf{R} - \frac{m_1}{m_1 + m_2} \mathbf{r} , \end{aligned}$$

and we define the relative displacement

$$\mathbf{r}(t) = \mathbf{r}_1(t) - \mathbf{r}_2(t)$$

to deal with one variable instead of two. The time derivative of the relative displacement is the relative velocity  $\mathbf{v}(t)$ .

In terms of  $\mathbf{r}(t)$ , Newton's second law takes special form

$$\mathbf{F}_{12} = m_* \frac{d^2 \mathbf{r}}{dt^2} ,$$

where

$$m_* = \frac{m_1 m_2}{m_1 + m_2}$$

is the reduced mass.

### Energy Conservation

The total energy in the two-body system is the sum of a kinetic term and a potential term. For the kinetic energy we have

$$T = \frac{1}{2} m_* v^2 + \frac{1}{2} (m_1 + m_2) V_0^2 ,$$

where we take  $V_0 = 0$  without loss of generality. For the potential energy we're stuck with just  $U(r)$ .

For the total energy, we write

$$E = T + U = \frac{1}{2} m_* v^2 + U(r) .$$

Take a single time derivative to find  $E$  to be constant

$$\begin{aligned} \frac{dE}{dt} &= \frac{1}{2} m_* \frac{d}{dt} (v^2) + \frac{d}{dt} U(r) \\ &= \frac{1}{2} m_* 2\mathbf{v} \cdot \frac{d\mathbf{v}}{dt} + \mathbf{v} \cdot \frac{d}{dr} (U(r)) \\ &= \mathbf{v} \cdot \left( m_* \frac{d\mathbf{v}}{dt} + \frac{d}{dr} (U(r)) \right) , \end{aligned}$$

because the parenthesized term is identically Newton's second law and resolves to zero.

### Angular Momentum

The angular momentum

$$\mathbf{L} = m_* \mathbf{r} \times \mathbf{v}$$

doesn't depend on  $U(r)$  at all, thus we recycle the constant of motion from planetary motion analysis:

$$L = m_* r^2 \omega ,$$

where  $\omega = d\theta/dt$ . Since  $L$  is constant, we know the motion to be planar.

## Polar Coordinates

In the polar coordinate system, the relative position, velocity, and acceleration vectors read

$$\begin{aligned}\mathbf{r} &= r \hat{\mathbf{r}} \\ \mathbf{v} &= \frac{dr}{dt} \hat{\mathbf{r}} + r\omega \hat{\boldsymbol{\theta}} \\ \mathbf{a} &= \left( \frac{d^2r}{dt^2} - r\omega^2 \right) \hat{\mathbf{r}} + \left( r \frac{d\omega}{dt} + 2 \frac{dr}{dt} \omega \right) \hat{\boldsymbol{\theta}}.\end{aligned}$$

The  $\hat{\boldsymbol{\theta}}$ -term in the acceleration is proportional to  $dL/dt$  and vanishes entirely, leaving a purely radial acceleration vector

$$\mathbf{a} = \left( \frac{d^2r}{dt^2} - \frac{L^2}{m_*^2 r^3} \right) \hat{\mathbf{r}}.$$

## 2.1 Effective Potential

In terms of the angular momentum  $L$ , the velocity vector can be written

$$\mathbf{v} = \frac{dr}{dt} \hat{\mathbf{r}} + \frac{L}{m_* r} \hat{\boldsymbol{\theta}},$$

meaning

$$v^2 = \left( \frac{dr}{dt} \right)^2 + \frac{L^2}{m_*^2 r^2}.$$

Feed this  $v^2$  into the energy conservation statement:

$$E = \frac{1}{2} m_* \left( \frac{dr}{dt} \right)^2 + \frac{L^2}{2m_* r^2} + U(r)$$

The latter two terms constitute the *effective potential energy*

$$U_{\text{eff}}(r) = U(r) + \frac{L^2}{2m_* r^2},$$

also known as the *centrifugal potential energy*, the gradient of which is the centrifugal force.

In terms of the effective potential, the total energy goes back down to two terms, one with time dependence and one with spatial dependence:

$$E = \frac{1}{2} m_* \left( \frac{dr}{dt} \right)^2 + U_{\text{eff}}(r)$$

### Problem 9

For the elliptical orbit of a planet, show for a given radius  $r_0$  that:

$$|U_{\text{eff}}(r_0)| = \frac{-Gm_1 m_2}{2r_0}$$

## 2.2 One-Dimensional Systems

In terms of the effective potential energy, the total energy is reduced to a one-dimensional system in the variable  $r$ . Taking this literally, let us study the generic one-dimensional system

$$E = \frac{1}{2} m \left( \frac{dx}{dt} \right)^2 + U(x)$$

to remove complications from planar motion.

Solving the above for the velocity, one writes

$$\frac{dx}{dt} = \pm \sqrt{\frac{2}{m} (E - U(x))}$$

to establish the equation of motion

$$t = \pm \sqrt{\frac{m}{2}} \int_{x_i}^{x_f} \frac{dx}{\sqrt{E - U(x)}}.$$

### Time-Reversal Symmetry

The  $\pm$  symbol in the equation of motion indicates *time-reversal symmetry* of the problem. Typically in one-dimensional systems, the *solution* to the equation of motion exhibits such symmetry, a stronger constraint than what we have. Supposing  $x(t)$  is a solution to the equation of motion, time-reversal symmetry implies that  $x_1(t) = x(t_0 - t)$  is also a solution that differs from original  $x(t)$  by an integration constant.

For most configurations, there exists at least one turning point  $t_*$  at which the velocity goes to zero. We exploit time-reversal symmetry to write an exact time-reversed-and-shifted equation

$$x_1(t) = x(2t_* - t).$$

Next, we note from function- and derivative matching that

$$\begin{aligned}x_1(t_*) &= x(t_*) \\ \frac{d}{dt} x_1(x(t_*)) &= -\frac{d}{dt} x(x(t_*)) = 0,\end{aligned}$$

and so on for higher derivatives. We may then drop the 1-subscript to get

$$x(t) = x(2t_* - t).$$

Shifting the above by  $t_*$ , the symmetric equation

$$x(t_* + t) = x(t_* - t)$$

emerges. In one dimension, the essence of time-reversal symmetry means that equations of motion are symmetric about turning points  $t_*$ .



### Trapped Particle

Potential energy functions  $U(x)$  that exhibit at least one local minimum can ‘trap’ a particle into an oscillatory pattern. Supposing  $x_i$  and  $x_f$  correspond to turning points in the motion, the oscillatory period is given by

$$T = \sqrt{2m} \int_{x_i}^{x_f} \frac{dx}{\sqrt{E - U(x)}}.$$

The quantity  $E - U(x)$  is always positive except at the turning points, at which the speed of the particle is instantaneously zero.

### Harmonic Oscillations

In the vicinity of a local energy minimum at  $x_*$ , the first- and second-derivatives of  $U(x_*)$  are

$$\begin{aligned} \frac{d}{dx}U(x_*) &= 0 \\ \frac{d^2}{dx^2}U(x_*) &= \lambda > 0, \end{aligned}$$

which allows  $U(x)$  to be approximated by Taylor series:

$$U(x) \approx U(x_*) + \frac{1}{2}\lambda(x - x_*)^2$$

Applying Newton’s second law, the corresponding equation of motion is

$$\frac{d^2}{dx^2}x(t) = -\frac{\lambda}{m}(x - x_*),$$

whose solution is known as the *harmonic oscillator*

$$x(t) = x_* + A \sin\left(\sqrt{\frac{\lambda}{m}}t - \phi_0\right).$$

The amplitude of oscillation is  $A$ , and the initial phase is contained in  $\phi_0$ .

### Unstable Equilibrium

An equilibrium point  $x_*$  exists at any local maximum of  $U(x)$ , however motion around such a point is unstable (non-oscillatory). To show this, reverse the sign on  $\lambda$  to arrive at the differential equation

$$\frac{d^2}{dx^2}x(t) = \frac{\lambda}{m}(x - x_*),$$

generally solved by

$$x(t) = x_* + Ae^{\lambda t} + Be^{-\lambda t}.$$

That is, the particle is pulled away from  $x_*$  and rides  $U(x)$  downhill.

## 2.3 Planar Orbits

Returning to the case of planar orbits, we can extrapolate all one-dimensional results to two dimensions by replacing  $x \rightarrow r$  and accounting for  $\theta(t)$  as a dynamic variable.

### Equations of Motion

In terms of the total energy  $E$ , the time evolution of the two-body system is given by

$$t(r) = \pm \sqrt{\frac{m_*}{2}} \int_{r_i}^{r_f} \frac{dr}{\sqrt{E - U_{\text{eff}}(r)}}.$$

An equation for  $\theta(t)$  is attained by integrating the angular momentum  $L = m_* r^2 \omega$  to write

$$\theta(t) = \theta_0 + \frac{L}{m_*} \int_0^t \frac{dt'}{(r(t'))^2}.$$

Switching to the  $r$  domain, the above is also written

$$\theta(r) = \pm \frac{L}{\sqrt{2m_*}} \int_{r_i}^{r_f} \frac{dr/r^2}{\sqrt{E - U_{\text{eff}}(r)}}.$$

### Apogee and Perigee

Supposing there exists a time  $t_*$  at which the radius  $r$  reaches a turning point (i.e.  $dr/dt = 0$ ), the corresponding point  $(r_*, \theta_*)$  in the plane is called the *apogee* if  $r$  is at a maximum, and the *perigee* if  $r$  is at a minimum.

Solutions to the  $\theta$ -equation occur in four explicit branches:

Apogee,  $\theta > \theta_*$

$$\theta = \theta_0 + \frac{L}{\sqrt{2m_*}} \int_{r_*}^r \frac{dr/r^2}{\sqrt{E - U_{\text{eff}}(r)}}$$

Apogee,  $\theta < \theta_*$

$$\theta = \theta_0 - \frac{L}{\sqrt{2m_*}} \int_{r_*}^r \frac{dr/r^2}{\sqrt{E - U_{\text{eff}}(r)}}$$

Perigee,  $\theta > \theta_*$

$$\theta = \theta_0 + \frac{L}{\sqrt{2m_*}} \int_r^{r_*} \frac{dr/r^2}{\sqrt{E - U_{\text{eff}}(r)}}$$

Perigee,  $\theta < \theta_*$

$$\theta = \theta_0 - \frac{L}{\sqrt{2m_*}} \int_r^{r_*} \frac{dr/r^2}{\sqrt{E - U_{\text{eff}}(r)}}$$

Evident in the above is the time-refersal symmetry about  $\theta_*$ , namely

$$r(\theta_* - \theta) = r(\theta_* + \theta).$$

### Bounded Orbits

When the potential energy  $U(x)$  contains a local minimum, a particle with a sufficiently low energy may become ‘trapped’ in the so-called *potential well*. Looking at the evolution of  $\theta$  between two extreme points (perigee to apogee or vice-versa), we have

$$\theta = \frac{L}{\sqrt{2m_*}} \int_{r_p}^{r_a} \frac{dr/r^2}{\sqrt{E - U_{\text{eff}}(r)}},$$

which is some number that is not generally a rational fraction of  $\pi$ . That is, we find that orbits are bounded aren’t necessarily repeated shapes, but may have a any (or an infinite) number of apogees and perigees. We will soon find there are two exceptions to this, where if the energy  $U$  has certain dependence on  $r$ , closed orbits are possible.

### Circular Orbit

The circular orbit is characterized by  $dr/dt = 0$ , or equivalently  $r(t) = r_0$ . The equation of motion for  $\theta(t)$  becomes trivial

$$\theta(t) = \theta_0 + \frac{Lt}{m_* r_0^2},$$

and the time  $T_0$  required for  $\theta(t) - \theta_0 = 2\pi$  corresponds to the period of the circular orbit:

$$T_0 = \frac{2\pi m_* r_0^2}{L}$$

As for the energy of a circular orbit, we have

$$E = \frac{1}{2} m_* \left( \frac{dr}{dt} \right)^2 + \frac{L^2}{2m_* r^2} + U(r),$$

which remains constant. Taking an  $r$ -derivative at  $r_0$  yields

$$0 = -\frac{L^2}{m_* r_0^3} + \frac{d}{dr} (U(r)) \Big|_{r_0},$$

or, in shorthand:

$$U'(r_0) = \frac{L^2}{m_* r_0^3}$$

Eliminate  $L$  from the above to write

$$U'(r_0) = m_* r_0 \omega^2 = \frac{m_* v_0^2}{r_0},$$

which is precisely the force ‘felt’ by an object constrained to uniform circular motion. (The force vector itself points to the center.)

We can eliminate  $L$  once more to express the period  $T$  of the circular orbit in terms of  $U'(r_0)$ :

$$T_0 = 2\pi \sqrt{\frac{m_* r_0}{U'(r_0)}}$$

#### Problem 10

Check that the circular orbit is described by

$$\frac{d}{dr} (U_{\text{eff}}(r)) \Big|_{r_0} = 0.$$

#### Problem 11

Show that Kepler’s law of equal areas hold for any central force, including straight-line motion.

## 3 Power Law Potential

Finally we must choose a particular form for the potential energy  $U(r)$ , thus we’ll pose a *central power law potential*

$$U(r) = -\frac{\Lambda}{r^\alpha},$$

where  $\Lambda$  is an arbitrary constant (positive or negative), and  $\alpha = 2$  reproduces the case for planetary motion. In the general case, we use

$$U_{\text{eff}}(r) = -\frac{\Lambda}{r^\alpha} + \frac{L^2}{2m_* r^2}$$

for the effective potential energy.

### 3.1 Circular Orbit

For orbits that have a nearly-circular radius  $r_0$ , we may approximate the effective potential energy via Taylor expansion in the vicinity  $r \approx r_0$ :

$$U_{\text{eff}}(r) = U_{\text{eff}}(r_0) + \frac{d}{dr} (U_{\text{eff}}(r)) \Big|_{r_0} (r - r_0) + \frac{d^2}{dr^2} (U_{\text{eff}}(r)) \Big|_{r_0} \frac{(r - r_0)^2}{2!} + \dots$$

### Stability

The first-order derivative term is identically zero by nature of the circular orbit. The second-order term must be done by brute force:

$$\begin{aligned} \frac{d^2}{dr^2} U_{\text{eff}}(r) \Big|_{r_0} &= \frac{d}{dr} \left( \frac{\Lambda \alpha}{r^{\alpha+1}} - \frac{L^2}{m_* r^3} \right) \Big|_{r_0} \\ &= -\frac{\Lambda \alpha (\alpha + 1)}{r_0^{\alpha+2}} + \frac{3L^2}{m_* r_0^4} \end{aligned}$$

Now, from the first-order equation we learn

$$\frac{\Lambda \alpha}{r_0^{\alpha+1}} = \frac{L^2}{m_* r_0^3},$$

where eliminating  $L^2$  in the second-order term now gives

$$\begin{aligned} \left. \frac{d^2}{dr^2} U_{\text{eff}}(r) \right|_{r_0} &= -\frac{\Lambda\alpha(\alpha+1)}{r_0^{\alpha+2}} + \frac{3\Lambda\alpha}{r_0^{\alpha+2}} \\ &= \frac{\Lambda\alpha(2-\alpha)}{r_0^{\alpha+2}} \\ &= \frac{L^2}{m_* r_0^4} (2-\alpha) . \end{aligned}$$

We can also write the angular frequency  $\omega_0$  in terms of the angular momentum via

$$\omega_0 = \frac{L}{m_* r_0^2} ,$$

and thus

$$\left. \frac{d^2}{dr^2} U_{\text{eff}}(r) \right|_{r_0} = m_* \omega_0^2 (2-\alpha)$$

Rewriting the Taylor expansion, we now have

$$U_{\text{eff}}(r) \approx U_{\text{eff}}(r_0) + m_* \omega_0^2 (2-\alpha) \frac{(r-r_0)^2}{2!} .$$

For all  $\alpha > 2$ , near-circular orbits are unstable, meaning particles with high enough energy will slip away to  $r \rightarrow \infty$ , whereas particles with sufficiently low energy or sufficiently low radius will inevitably collapse to  $r = 0$ . For  $\alpha < 2$ , the system corresponds to a one-dimensional harmonic oscillator in  $r$ , thus near-circular orbits are stable. The angular frequency in the  $r$ -variable is given by

$$\omega_r = \omega_0 \sqrt{2-\alpha} ,$$

implying that periodic closed orbits occur when  $\sqrt{2-\alpha}$  is a rational number. Conveniently we'll see that the Coulomb and gravitational potentials ( $\alpha = 1$ ), along with the harmonic oscillator ( $\alpha = -2$ ) each produce closed orbits not limited to circles. The next closed orbit corresponds to  $\alpha = -7$ .

### Period

In terms of  $\omega_0$ , we can write the period  $T_0$  of a circular orbit. Start with the definition  $\omega T = 2\pi$ , we have

$$T_0 = \frac{2\pi}{\omega_0} = \frac{2\pi m_* r_0^2}{L}$$

### Harmonic Potential

The *harmonic potential* is defined by

$$U(r) = \Lambda r^2 .$$

As a central force, all motion is confined to a plane and thus we separate into components as

$$U(r) = \Lambda (x^2 + y^2) .$$

Using  $F_x = -\partial U / \partial x$  and similar for the  $y$ -component, the above implies a pair of independent one-dimensional differential equations

$$\begin{aligned} \frac{d^2}{dt^2} x(t) &= -\omega^2 x(t) \\ \frac{d^2}{dt^2} y(t) &= -\omega^2 y(t) , \end{aligned}$$

where  $\omega = \sqrt{2\Lambda/m_*}$ .

General solutions to the above are trigonometric, namely

$$\begin{aligned} x(t) &= A_x \cos(\omega t - \phi_x) \\ y(t) &= A_y \cos(\omega t - \phi_y) , \end{aligned}$$

where  $A_{x,y}$  and  $\phi_{x,y}$  are determined from initial conditions.

We can do away with the  $\phi_x$ -term by placing the particle at  $A_x$  at  $t = 0$  and defining the  $x$ -axis to pass through that point. Then, the  $y$ -component of the position must be zero, telling us  $\phi_y = \pi/2$ . Finally, we find a closed equation for elliptical orbits with the origin at the center:

$$\begin{aligned} x(t) &= A_x \cos(\omega t) \\ y(t) &= A_y \sin(\omega t) \end{aligned}$$

The envelopes of positions draws an ellipse:

$$\frac{x^2}{A_x^2} + \frac{y^2}{A_y^2} = 1$$

## 3.2 Dimensionless Variables

For a power law potential  $U(r) = -\Lambda/r^\alpha$ , we can find a circular orbit characterized by  $r = r_0$  that minimizes  $U_{\text{eff}}(r)$  at  $r_0$ . The period of such an orbit is  $T_0$ .

Let us now replace quantities of radius, energy, and time units with dimensionless variables by the following substitutions:

$$\begin{aligned} \rho(t) &= \frac{r(t)}{r_0} \\ \mathcal{E} &= \frac{E}{|U_{\text{eff}}(r_0)|} \\ \tau &= \frac{t}{T_0} = \frac{Lt}{2\pi m_* r_0^2} \end{aligned}$$

We bring  $\Lambda$  into the mix by recalling

$$\frac{L^2}{m_* r_0^2} = \frac{\Lambda\alpha}{r_0^\alpha}$$

for circular orbits, and it further follows that

$$|U_{\text{eff}}(r_0)| = \frac{L^2}{2m_*r_0^2} \left| \frac{2-\alpha}{\alpha} \right|.$$

### Problem 12

For a planet on an elliptical orbit with semi-major axis  $a$ , use

$$E = \frac{-Gm_1m_2}{2a}$$

to show that the eccentricity is given by

$$e = \sqrt{1 + \mathcal{E}}.$$

### Problem 13

For a planet on an elliptical orbit with semi-major axis  $a$  and semi-minor axis  $b$ , show that

$$\frac{b}{a} = \sqrt{-\mathcal{E}}.$$

If the orbit is hyperbolic, show instead that

$$\frac{b}{a} = \sqrt{\mathcal{E}}.$$

## Equations of Motion

The equations of motion

$$\begin{aligned} t(r) &= \pm \sqrt{\frac{m_*}{2}} \int_{r_i}^{r_f} \frac{dr}{\sqrt{E - U_{\text{eff}}(r)}} \\ \theta(r) &= \pm \frac{L}{\sqrt{2m_*}} \int_{r_i}^{r_f} \frac{dr/r^2}{\sqrt{E - U_{\text{eff}}(r)}} \end{aligned}$$

must be recast in dimensionless variables.

Staying in the special case  $\Lambda > 0$ ,  $\alpha < 2$ , proceed by simplifying the radical term first:

$$\begin{aligned} E - U_{\text{eff}}(r) &= E + \frac{\Lambda}{r^\alpha} - \frac{L^2}{2m_*r^2} \\ &= \frac{\mathcal{E}\Lambda\alpha}{2r_0^\alpha} \left( \frac{2-\alpha}{\alpha} \right) + \frac{\Lambda}{r_0^\alpha \rho^\alpha} - \frac{\Lambda\alpha}{2r_0^\alpha \rho^2} \\ &= \left( \frac{\Lambda\alpha}{2r_0^\alpha} \right) ((2-\alpha)\mathcal{E}/\alpha + (2/\alpha)/\rho^\alpha - 1/\rho^2) \end{aligned}$$

Substituting carefully, one finds

$$\begin{aligned} \tau &= \pm \frac{1}{2\pi} \int_{\rho_i}^{\rho_f} \frac{d\rho}{\sqrt{(2-\alpha)\mathcal{E}/\alpha + (2/\alpha)/\rho^\alpha - 1/\rho^2}} \\ \theta &= \pm \int_{\rho_i}^{\rho_f} \frac{d\rho/\rho^2}{\sqrt{(2-\alpha)\mathcal{E}/\alpha + (2/\alpha)/\rho^\alpha - 1/\rho^2}}. \end{aligned}$$

Note that solutions to

$$0 = (2-\alpha)\mathcal{E}/\alpha + (2/\alpha)/\rho^\alpha - 1/\rho^2$$

indicate all apogees and perigees in the motion.

## 3.3 Inverse Square Attraction

The attractive power law potential with  $\Lambda > 0$  and  $\alpha = 1$  corresponds to the gravitational force and the attractive static electric force. Such a potential naturally hosts a circular orbit with:

$$\begin{aligned} r_0 &= \frac{L^2}{\Lambda m_*} \\ T_0 &= \frac{2\pi m_* r_0^2}{L} \\ |U_{\text{eff}}| &= \frac{L^2}{2m_* r_0^2} = \frac{\Lambda^2 m_*}{2L^2} \end{aligned}$$

### Spatial Dynamics

The equations of motion simplify significantly with  $\alpha = 1$ . For the  $\theta$ -equation, we have

$$\theta = \pm \int_{\rho_i}^{\rho_f} \frac{d\rho/\rho^2}{\sqrt{\mathcal{E} + 2/\rho - 1/\rho^2}}.$$

Let  $\xi = 1/\rho$  to find

$$\theta = \pm \int \frac{-d\xi}{\sqrt{\mathcal{E} - (\xi - 1)^2 + 1}},$$

and then let  $\beta = \xi - 1$  to get

$$\theta = \pm \int \frac{-d\beta}{\sqrt{\mathcal{E} - \beta^2 + 1}}.$$

Factor  $\sqrt{1 + \mathcal{E}}$  from the denominator and also let  $\gamma = \beta/\sqrt{1 + \mathcal{E}}$ :

$$\begin{aligned} \theta &= \pm \int \frac{-d\beta}{\sqrt{1 + \mathcal{E}} \sqrt{1 - \beta^2/(1 + \mathcal{E})}} \\ &= \pm \int \frac{-d\gamma}{\sqrt{1 - \gamma^2}} \end{aligned}$$

Next, let  $\gamma = \cos(\psi)$  to find

$$\theta = \pm \int \frac{\sin(\psi) d\psi}{\sin(\psi)} = \pm \int d\psi.$$

The remaining integral has a trivial solution

$$\theta = \theta_0 \pm \psi,$$

and undoing all substitutions gives

$$\theta = \theta_0 \pm \arccos\left(\frac{1/\rho - 1}{\sqrt{1 + \mathcal{E}}}\right),$$

where the integration constant  $\theta_0$  is an ignorable rotation in the plane. Continue solving for  $\rho$  to get the equation of a conic section:

$$\rho = \frac{1}{1 + \sqrt{1 + \mathcal{E}} \cos(\theta)}$$

**Eccentricity**

The combination  $\sqrt{1+\mathcal{E}}$  is none other than the eccentricity of the orbit:

$$e = \sqrt{1+\mathcal{E}}$$

From what we know of conic sections, recall that  $e = 1$  makes a parabola,  $e < 1$  makes an ellipse, and  $e > 1$  makes a hyperbola. In terms of the dimensionless energy  $\mathcal{E}$ , this also means:

$$\begin{aligned}\mathcal{E} = 0 &\rightarrow \text{parabola} \\ \mathcal{E} < 0 &\rightarrow \text{ellipse} \\ \mathcal{E} > 0 &\rightarrow \text{hyperbola}\end{aligned}$$

**Conserved Quantities**

As a special case of the two-body central potential system, we're aware that the inverse-square attraction supports conservation of energy  $E$  and conservation of angular momentum  $L$ .

Also conserved is the Runge-Lorenz vector

$$\mathbf{Z} = \mathbf{v} \times \mathbf{L} - \Lambda \hat{\mathbf{r}},$$

which fixes the orientation of the total orbit in its plane of motion. Take a time derivative to quickly prove  $\mathbf{Z}$  is constant:

$$\begin{aligned}\frac{d}{dt}\mathbf{Z} &= \frac{d\mathbf{v}}{dt} \times \mathbf{L} + \mathbf{v} \times \frac{d\mathbf{L}}{dt} - \Lambda \frac{d\hat{\mathbf{r}}}{dt} \\ &= -\frac{1}{m_*} \frac{\Lambda}{r^2} \hat{\mathbf{r}} \times (\mathbf{r} \times m_* \mathbf{v}) - \Lambda \frac{d}{dt} \left( \frac{\mathbf{r}}{r} \right) \\ &= \Lambda \left( \frac{-(\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \mathbf{v}) - \mathbf{v}(\hat{\mathbf{r}} \cdot \hat{\mathbf{r}}))}{r} - \frac{\mathbf{v}}{r} + \frac{\hat{\mathbf{r}}}{r} (\hat{\mathbf{r}} \cdot \mathbf{v}) \right) \\ &= 0\end{aligned}$$

Being constant, we're free to evaluate  $\mathbf{Z}$  anywhere on the orbit. Choosing a perigee at  $\mathbf{r}_p = r_p \hat{\mathbf{x}}$  where  $\mathbf{v}_p \cdot \mathbf{r}_p = 0$ , we find:

$$\begin{aligned}\mathbf{Z} &= \mathbf{v}_p \times (\mathbf{r}_p \times m_* \mathbf{v}_p) - \Lambda \hat{\mathbf{r}}_p \\ &= m_* \mathbf{r}_p (\mathbf{v}_p \cdot \mathbf{v}_p) - m_* \mathbf{v}_p (\mathbf{r}_p \cdot \mathbf{r}_p) - \Lambda \hat{\mathbf{r}}_p \\ &= \left( \frac{L^2}{m_* r_p} - \Lambda \right) \hat{\mathbf{r}}_p = \Lambda \left( \frac{r_0}{r_p} - 1 \right) \hat{\mathbf{x}} \\ &= \Lambda \left( \frac{1}{\rho_p} - 1 \right) \hat{\mathbf{x}} = \Lambda \left( 1 + \sqrt{1+\mathcal{E}} - 1 \right) \hat{\mathbf{x}} \\ \mathbf{Z} &= \Lambda e \hat{\mathbf{x}}\end{aligned}$$

**Conic Trajectory**Problem 14

Derive the dimensionless Runge-Lorenz vector equation

$$\hat{\mathbf{r}} + e \hat{\mathbf{x}} = \frac{\mathbf{v} \times \mathbf{L}}{\Lambda},$$

and then project  $\mathbf{r}$  into each side to recover the equation of a conic section, namely

$$r = \frac{r_0}{1 + e \cos(\theta)}.$$

**Temporal Dynamics**

The integral for the dimensionless time  $\tau$  is straightforwardly solved with  $\alpha = 1$ . Begin with

$$\tau = \pm \frac{1}{2\pi} \int_{\rho_i}^{\rho_f} \frac{d\rho}{\sqrt{\mathcal{E} + 2/\rho - 1/\rho^2}}$$

and assume  $\mathcal{E} \neq 0$ . Simplify a bit to get

$$\tau = \pm \frac{\sqrt{\mathcal{E}}}{2\pi e} \int_{\rho_i}^{\rho_f} \frac{\rho d\rho}{\sqrt{\mathcal{E}(\rho\sqrt{\mathcal{E}} + 1/\sqrt{\mathcal{E}})^2/e^2 - 1}}.$$

Let  $\xi = \sqrt{\mathcal{E}}(\rho\sqrt{\mathcal{E}} + 1/\sqrt{\mathcal{E}})/e$  so that  $d\xi = d\rho\mathcal{E}/e$  and

$$\rho d\rho = e \left( \frac{\xi e - 1}{\mathcal{E}^2} \right) d\xi,$$

giving

$$\tau = \pm \frac{1}{2\pi \mathcal{E}^{3/2}} \int \frac{(\xi e - 1)}{\sqrt{\xi^2 - 1}} d\xi.$$

So far we've been a bit loose with the sign on  $\mathcal{E}$ . For  $\mathcal{E} > 0$ , everything stays as-is. However for  $\mathcal{E} < 0$ , we have to propagate  $\mathcal{E} \rightarrow -|\mathcal{E}|$  through the calculation. Maintaining both channels, we have:

$$\begin{aligned}\tau_{\mathcal{E}>0} &= \pm \frac{1}{2\pi |\mathcal{E}|^{3/2}} \int \frac{(\xi e - 1)}{\sqrt{\xi^2 - 1}} d\xi \\ \tau_{\mathcal{E}<0} &= \pm \frac{1}{2\pi |\mathcal{E}|^{3/2}} \int \frac{(\xi e - 1)}{\sqrt{1 - \xi^2}} d\xi\end{aligned}$$

Let

$$\begin{aligned}\xi_{\mathcal{E}>0} &= \cosh(\psi) \\ \xi_{\mathcal{E}<0} &= \cos(\psi)\end{aligned}$$

and each integral becomes trivial, setting arbitrary integration constants to zero:

$$\begin{aligned}\tau_{\mathcal{E}>0} &= \pm \frac{1}{2\pi |\mathcal{E}|^{3/2}} (e \sinh(\psi) - \psi) \\ \tau_{\mathcal{E}<0} &= \pm \frac{1}{2\pi |\mathcal{E}|^{3/2}} (\psi - e \sin(\psi))\end{aligned}$$

The period of an elliptical orbit corresponds to one full cycle in  $\psi$ , i.e.  $0 \leq \psi < 2\pi$ . For this we have

$$\tau_{\text{period}} = 2(\tau_\pi - \tau_0) = |\mathcal{E}|^{-3/2}.$$

#### Problem 15

Use

$$\tau = \frac{t}{T_0} = \frac{Lt}{2\pi m_* r_0^2}$$

and let  $\tau = |\mathcal{E}|^{-3/2}$ . Solve for  $t = T$  to recover Kepler's third law for elliptical orbits.

#### Radial Component

Using the  $\rho$ -substitution from the above integral, namely

$$\begin{aligned} \rho_{\mathcal{E}>0} &= \frac{e\xi - 1}{\mathcal{E}} \\ \rho_{\mathcal{E}<0} &= \frac{e\xi - 1}{-|\mathcal{E}|}, \end{aligned}$$

we get solutions for  $\rho(\psi)$ :

$$\begin{aligned} \rho_{\mathcal{E}>0} &= \frac{e \cosh(\psi) - 1}{\mathcal{E}} \\ \rho_{\mathcal{E}<0} &= \frac{1 - e \cos(\psi)}{|\mathcal{E}|} \end{aligned}$$

The perigee corresponds to  $\psi = 0$ . For  $\mathcal{E} < 0$ , the apogee is at  $\psi = \pi$ .

#### Zero-Energy Case

Returning to the equations of motion for  $\tau, \theta$  with  $\mathcal{E} = 0$  and  $\alpha = 1$ , we have

$$\begin{aligned} \tau &= \pm \frac{1}{2\pi} \int_{\rho_i}^{\rho_f} \frac{\rho d\rho}{\sqrt{2\rho - 1}} \\ \theta &= \pm \int_{\rho_i}^{\rho_f} \frac{d\rho/\rho}{\sqrt{2\rho - 1}}, \end{aligned}$$

resolving to, discarding the integration constants:

$$\begin{aligned} \tau &= \pm \frac{1}{6\pi} \sqrt{2\rho - 1} (\rho + 1) \\ \theta &= \pm 2 \arctan \left( \sqrt{2\rho - 1} \right) \end{aligned}$$

### 3.4 Inverse Square Repulsion

Consider the central potential given by

$$U = \frac{\Lambda}{r},$$

as one finds with the repulsive Coulomb force. This is the same as the inverse square attractive case with the modification  $\Lambda \rightarrow -\Lambda$ , and the recipe for the equations of motion is essentially the same. Some key results are:

$$\begin{aligned} \rho &= \frac{1}{-1 + \sqrt{1 + \mathcal{E} \cos(\theta)}} \\ \tau &= \pm \frac{1}{2\pi |\mathcal{E}|^{3/2}} (e \sinh(\psi) + \psi) \\ \rho &= \frac{1}{\mathcal{E}} (e \cosh(\psi) + 1) \end{aligned}$$

# Chapter 3

## Thermodynamics

### 1 Heat and Energy

#### Thermodynamic System

A *thermodynamic system* is any collection of parts that permits energy transfer between its members. A closed thermodynamic system allows no energy or material transfer across its boundary. Conversely, an open thermodynamic system does allow such interactions with its environment.

#### Temperature

*Temperature* is a scale used for quantifying the amount of ‘hotness’ in a system. We’ll soon build up the vocabulary to create a sophisticated definition of temperature, but it suffices for now to say:

*Temperature is a quantity that eventually becomes the same for two systems after sustained contact.*

Typical temperature scale units, namely Fahrenheit and Centigrade, aren’t defined in fundamental terms of length, space, or time.

#### Problem 1

At atmospheric pressure (also known as *standard pressure*), liquid water boils at 212°F and freezes at 32°F. On the centigrade scale, these temperatures are 100°C and 0°C, respectively. Calculate the one temperature at which the Fahrenheit and centigrade scales, assumed linear with temperature, are in agreement. Answer:  $-40^\circ\text{F} = -40^\circ\text{C}$

#### Zeroth Law

Sustained contact between two systems can lead to a state called *thermal equilibrium*, achieved when there is zero net energy flowing between each system. This idea is also contained in the *zeroth law of thermodynamics*:

*If system A and system B are each in equilibrium with system C, then A and B are in equilibrium with each other.*

#### Quasistatic Approximation

The *quasistatic approximation* is the limit when thermodynamic processes occur ‘slowly’ enough such the whole substance maintains instantaneous equilibrium throughout any process.

### 1.1 Matter and Temperature

#### Thermal Expansion

The volume of an object is subject to its temperature. Adding heat usually causes the volume to increase, an effect called *thermal expansion*.

Taking a one-dimensional example, consider a thin metal rod of length  $L_0$  and initial temperature  $T_0$ . An external heat source changes the rod’s temperature by  $\Delta T$ , and the length is observed to change by  $\Delta L$ . Restoring the temperature to  $T_0$ , the length restores to  $L_0$ . It follows that a linear ‘law’ for thermal expansion can be written as

$$L = L_0 + \alpha L_0 \Delta T, \quad (3.1)$$

where the parameter  $\alpha$  is the *linear thermal expansion coefficient*, measuring typically around  $10^{-5}$  per degree centigrade. The temperature change  $\Delta T$  may be positive or negative, and the rod expands or contracts, respectively.

Thermal expansion occurs in more than one spatial dimensions. For two dimensions, consider a plate of area  $L_0 \times W_0$ . With a change in temperature, the area of the plate becomes

$$\begin{aligned} A &= L_0 W_0 (1 + \alpha \Delta T)^2 \\ &\approx L_0 W_0 (1 + 2\alpha \Delta T). \end{aligned} \quad (3.2)$$

For small temperature displacements,  $\alpha^2 \Delta T^2$  is a reasonably small contribution to thermal expansion and is ignored to first-order approximation. Thus the area scales linearly with temperature, with effective expansion factor  $2\alpha$ .

For three dimensions, the effective expansion constant is  $\beta = 3\alpha$ . If the volume of the object is  $V_0$ , this means

$$V \approx V_0 (1 + \beta \Delta T) . \quad (3.3)$$

### Problem 2

A circular piece with diameter  $d$  is removed from a room-temperature sheet of aluminum. If the sheet is heated in an oven, how does the area of the hole change with temperature? Does the hole increase or decrease in area? Answer:  $\Delta A = \pi d^2 \alpha \Delta T / 2$ , increasing.

### Problem 3

On a cool  $4^\circ\text{C}$  morning, a driver fills his aluminum gasoline tank to the full capacity of 106.0 L. That evening, he checks the fuel level and finds 103.4 L remaining in the tank. The coefficient of volume expansion for gasoline is  $9.5 \times 10^{-4}/^\circ\text{C}$ , and for aluminum is  $7.25 \times 10^{-5}/^\circ\text{C}$ . What was the maximum temperature reached by the fuel tank during the day? Answer:  $32.70^\circ\text{C}$

### Problem 4

Consider a metal rod having a thermal expansion coefficient that varies with temperature such that  $\alpha(T) = A + BT + CT^2$ . Derive a formula for the length of the material as a function of temperature change. Answer:

$$\Delta L = L_0 (A\Delta T + B\Delta T^2/2 + C\Delta T^3/3)$$

## Thermal Stress

An object confined in space may not be able to physically undergo thermal expansion (or contraction), in which case the object undergoes *thermal stress*.

Suppose a thin metal rod of fixed length  $L_0$  is held between two clamps at temperature  $T_0$  with no initial forces on the ends of the rod. If the temperature changes, the rod ‘wants’ to obey the thermal expansion Equation (3.1), written here as

$$\frac{\Delta L}{L_0} = \alpha \Delta T ,$$

where  $\alpha$  is the linear thermal expansion coefficient.

Meanwhile, the Young’s modulus for the rod is defined as  $Y = (F/A)/(\Delta L/L_0)$ , so we write

$$\frac{\Delta L}{L_0} = \frac{F}{AY} ,$$

where  $F$  is the linear tension in the rod (positive or negative) and  $A$  is the cross-sectional area. Since  $\Delta L$  must be zero, we therefore have

$$\frac{F}{A} = -Y\alpha\Delta T . \quad (3.4)$$

## 1.2 Thermal Energy

The phenomenon of ‘heat’ occurs as a consequence of some type of energy expense: mechanical, chemical, electrical, nuclear, etc. We define *thermal energy*, denoted  $Q$ , as the broad subset of energies and potentials that couple strongly to temperature. Like all other energies in physics, thermal energy must be conserved.

It was known to Sir James Joule (1818-1889) and his contemporaries that the amount of work required to raise the temperature of water is directly proportional to the temperature change. Energy was measured in calories, where one *calorie* (c) is the amount of energy required to raise the temperature of one gram of water by one degree centigrade. (One food calorie, denoted with a capital C, is 1000 ordinary calories.)

Experiments conducted by Joule found that one calorie equals 4.186 energy units in the SI system, also known as Joules. Contemporary to this is the Btu, or *British thermal unit*, being  $252 \text{ cal} = 1055 \text{ J}$ . The Btu is defined as the amount of energy required to raise one pound of water by one degree Fahrenheit.

## Specific Heat

A small thermal energy quantity  $dQ$  transferred to a substance of mass  $m$  (without changing the phase) is linearly proportional to the change in temperature. This means we write

$$c = \frac{1}{m} \frac{dQ}{dT} , \quad (3.5)$$

where the proportionality constant  $c$  is the *specific heat* of the substance. Equation (3.5) can often be integrated in the variable  $T$ , giving a more familiar statement

$$Q = mc\Delta T . \quad (3.6)$$

A typical solid metal has  $c$  around 300 J per kilogram of material per degree centigrade. In the same units, liquid water has  $c = 4187$ , frozen water has  $c = 2108$ , and water vapor has  $c = 1996$ .



## Heat Capacity

The product of mass and specific heat yields the *heat capacity*:

$$C = mc \quad (3.7)$$

Like specific heat, the heat capacity is proportional to Joules per degree centigrade, but the notion of ‘per kilogram of material’ has been multiplied away. Heat capacity refers to the whole object.

## 1.3 Phases of Matter

*Phase* is a term synonymous with ‘state of matter’, used for classifying the overall spatial arrangement and dynamics of the particles in a substance. Common phases of matter are solid, liquid, and gas - but the list doesn’t stop there. More exotic phases such as plasmas and liquid crystals occur in nature (and the laboratory).

The phase of a given substance is chiefly determined by (i) the surrounding temperature, and (ii) the surrounding pressure. This is visualized by using a *phase diagram*, which comes in two flavors: *PT* and *PV*, standing for a pressure-temperature plot or pressure-volume plot, respectively.

### PT Diagram

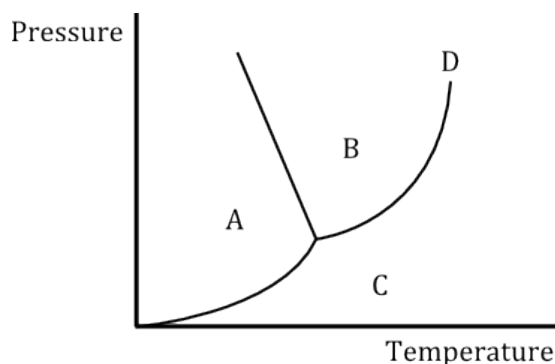


Figure 3.1: *PT* phase diagram.

Figure 3.1 illustrates a typical *PT* diagram for a typical substance (water for example). A small enough ‘parcel’ of a substance occupies just one point in the phase diagram at a given time, and the parcel’s ‘trajectory’ in a phase diagram is continuous over time, but not necessarily smooth.

Boundaries between regions in the phase diagram are associated with abrupt changes in the phase:

- Region *A* has low temperature and high pressure, corresponding to the solid state.

- Region *B* has moderate temperature and moderate pressure, corresponding to the liquid state.
- Region *C* has high temperature and low pressure, corresponding to the gaseous state.
- Region *D* indicates the supercritical state, a phase mixture of liquid and gas.
- Solid lines are boundaries that separate two phases.
- The junction of regions *A*, *B*, *C* is called the *triple point*.

### PV Diagram

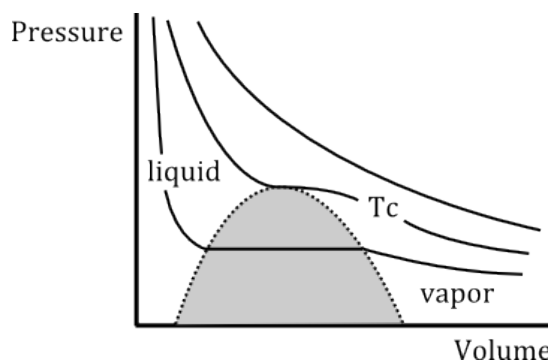


Figure 3.2: *PV* phase diagram.

A variation of the *PT* diagram is the *PV* diagram, where the volume replaces temperature on the horizontal axis. Figure 3.2 illustrates a typical *PV* diagram for another typical substance, excluding the solid state. The contour curves are called *isotherms*, having constant temperature. The shaded area under the dotted arch represents the liquid-vapor equilibrium phase. The isotherm  $T_C$  is the *critical temperature*.

### Mixtures and Dalton’s Law

A mixture of gases is itself a gas and may be treated as a unit. For instance, if a pressurized vessel holds a mixture of helium and nitrogen, then the gases are fully mixed, sharing the same volume and same temperature.

Each element also makes its own contribution to the pressure, called a *partial pressure*, where the total pressure  $P$  is  $P = P_{He} + P_{Ni}$  for the example on hand. This is known as Dalton’s law. In general, the law of partial pressures reads

$$P = \sum_j P_j, \quad (3.8)$$

where index  $j$  sums over the species in the mixture.

## Latent Heat

Changing the temperature or pressure of a substance causes some shift in the phase diagram. Crossing the boundary between any two regions (see Figure 3.1) corresponds to a *phase change*. At such a boundary, molecular order of the substance changes radically, which involves an energy change at the *chemical* level.

Now comes an important point about latent heat. For a substance *on* a phase boundary at a given pressure, all energy added or removed from the substance contributes to phase change with the temperature remaining constant.

To illustrate, consider a glass containing an ice + water mixture having initial temperature  $0^\circ\text{C}$ , the freezing point of water. Placed in a room-temperature environment, the mixture steadily absorbs heat from the surroundings. Does the temperature of the ice + water mixture increase? *No*, not for a while. Rather, any new energy added to the system contributes to melting the ice. Only when the ice is melted will the system's temperature begin to increase. The same experiment works in reverse: if instead the ice + water mixture were placed in a frigid  $-100^\circ\text{C}$  environment, the temperature would remain  $0^\circ\text{C}$  until all liquid water phase changes to ice. Only after this point would the overall temperature begin to plunge. (Of course, this all assumes that water is a perfect conductor of heat.)

During a phase change, the thermal energy of a substance is not governed by  $Q = mc\Delta T$  because  $\Delta T$  is zero during the change. Instead, the change in energy is called *latent heat*, which is proportional to the mass of material being changed:

$$Q = mL_\alpha \quad (3.9)$$

The amount of mass that changes phase per unit energy is a constant denoted  $L_\alpha$ , where subscript  $\alpha$  denotes which phase boundary is being crossed.

Subscript  $\alpha = v$  stands for ‘vaporization’, corresponding to the liquid-gas boundary, and  $\alpha = f$  stands for ‘fusion’, corresponding to the solid-liquid boundary. Water at atmospheric pressure has  $L_v = 2.256 \times 10^6 \text{ J/kg}$  and  $L_f = 3.34 \times 10^5 \text{ J/kg}$ .

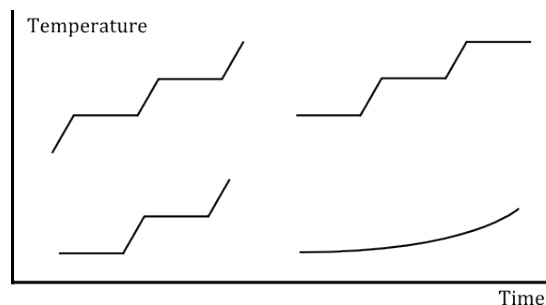


Figure 3.3: Temperature curves for tea kettle problem.

### Problem 5

A tea kettle is filled with ice at  $-10^\circ\text{C}$  and placed on a burner that is steadily getting hotter. Over a long enough time, the kettle empties due to evaporation. Of the four curves drawn in Figure 3.3, which best represents the temperature inside the kettle as a function of time? Use the quasistatic approximation. Answer: Top-left

### Problem 6

How much ice at  $0^\circ\text{C}$  must be added to a liter of water at  $80^\circ\text{C}$  so as to end up with all liquid at  $20^\circ\text{C}$ ? Answer:

$$\frac{m_{\text{ice}}}{m_0} = \frac{80^\circ\text{C} - 20^\circ\text{C}}{20^\circ\text{C} + (L_f/c)_{\text{water}}}$$

### Problem 7

A 15 g ice cube at  $0^\circ\text{C}$  is mixed with 2 g of steam at  $100^\circ\text{C}$  in an isolated container. What is the final state of the system?

Answer: (i) Since  $m_{\text{steam}}L_v - m_{\text{ice}}L_f < 0$ , all steam condenses, releasing 4512 J, which melts 13.51 g of ice, leaving 1.49 g in the solid state. (ii) Next, the 2 g of hot water must come to equilibrium with the melted ice, giving  $0 = 2(x - 100^\circ\text{C}) + 13.51x$ , where  $x$  solves to  $12.9^\circ\text{C}$ . (iii) Finally, let 15.51 g of water at  $12.9^\circ\text{C}$  come to equilibrium with the remaining ice, giving  $0 = 15.51(y - 12.9^\circ\text{C}) + 1.49L_f/c$ . Solving for  $y$ , the final system has 17 g of water at about  $5^\circ\text{C}$ .

### Problem 8

A 20 g ice cube at  $-10^\circ\text{C}$  is mixed with 2 g of steam at  $100^\circ\text{C}$  in an isolated container. What is the final state of the system?

Answer: (i) Energy required to warm ice to  $0^\circ\text{C}$ : 422 J. (ii) Amount of steam condensed to accomplish this: 0.187 g. (iii) Energy required to melt ice: 6680 J. (iv) Energy released by remaining steam condensation: 4090 J. (v) Energy released from cooling 2 g of water from  $100^\circ\text{C}$  to  $0^\circ\text{C}$ : 837 J. (vi) Energy available to melt ice: 4927 J. (vii) Mass of ice melted: 14.8 g. (viii) Final state has about 5 g of ice and 17 g of water at  $0^\circ\text{C}$ .

## 1.4 Heat Transfer

### Conduction

*Conduction* is heat transfer due to microscopic motions of particles, where more rapidly-moving particles exchange kinetic energy by collision with ‘colder’ particles. A material’s affinity to conduct heat in this way is the *thermal conductivity*,  $k$ , measured in Watts per meter per degree centigrade. (Incidentally, most materials that easily conduct electric currents also have high thermal conductivity.)

Consider two objects  $H$  and  $C$  that are maintained at constant temperatures  $T_H$  and  $T_C$ , respectively. The ‘hotter’ object  $H$  is connected to the ‘colder’ object  $C$  by a conductor having cross-sectional area  $A$  and thermal conductivity  $k$ .

From ordinary classical mechanics, we can write the rate of energy flow  $dQ/dt$  across the conductor:

$$\frac{dQ}{dt} = -\frac{d}{dt} \int \nabla U \cdot d\mathbf{x} = - \int \nabla U \cdot \frac{d\mathbf{x}}{dt}$$

The gradient  $\nabla U$  term is proportional to (i) the temperature difference  $\Delta T = T_C - T_H$ , and (ii) the conductor cross section  $A$ . The  $d\mathbf{x}/dt$  term represents the rate and direction of energy flow across  $A$ , proportional to the thermal conductivity  $k$ . The differential equation for heat conduction is therefore

$$\frac{dQ}{dt} = -kA\Delta T, \quad (3.10)$$

where  $\Delta T$  is known as the *temperature gradient*. The negative sign reminds that heat flows from hot to cold.

### R-Value

The  $R$ -value of a material is equal to the thickness (along the direction of heat flow) divided by the conductivity:

$$R = \frac{L}{k}$$

One inch of wood has  $R \approx 1$ . Typical New England houses have  $R \approx 19$  for the walls and  $R \approx 30$  for the roof. The  $R$ -value is an additive quantity, i.e.  $R_{\text{eff}} = R_1 + R_2 + \dots$

---

#### Problem 9

The walls of a house are insulated with 2.0 cm of Styrofoam ( $k_{\text{SF}} = 0.01 \text{ W/mK}$ ), and 15.0 cm of fiberglass ( $k_{\text{FG}} = 0.04 \text{ W/mK}$ ). The Styrofoam is on the exterior of the house. The outside temperature is  $0^\circ\text{C}$ , and the interior of the house is maintained

at  $20^\circ\text{C}$ . (i) Calculate the temperature on the SF-FG interface. (ii) What is the rate of heat transfer per  $\text{m}^2$  through both layers of insulation? (iii) Which provides greater net insulation, an additional 1.0 cm of Styrofoam, or an additional 5.0 cm of fiberglass? Answer:  $6.96^\circ\text{C}$ ,  $3.5 \text{ W}$ , fiberglass.

#### Problem 10

Inside a conductive cylinder of length  $L$  and radius  $R$ , heat flows radially from the axis  $r = 0$  toward the wall at  $R$  with  $T(0) > T(R)$ . Calculate the thermal energy flow rate between any two radii  $r_1$  and  $r_2$  in cylinder. Answer:

$$dQ/dt = k2\pi RL(T_1 - T_2) / \ln(r_2/r_1)$$

#### Problem 11

If a tank of water initially at  $0^\circ\text{C}$  is left in very cold conditions (assume  $-10^\circ\text{C}$ ), a sheet of ice forms on the water surface and grows downward over time. Supposing all heat transfer takes place through the ice, and not through the container walls: (i) Determine the thickness  $Z$  of the ice as a function of time  $t$ . (ii) Calculate the thickness of the ice sheet that will form in one day. (iii) If the tank is 50 cm deep, how many days does it take to freeze all of the water? (iv) If the tank is 10 m deep, how many days does it take to freeze all of the water? Answer: (i)  $Z = (\Delta T 2k / (\rho L_f))^{1/2} \sqrt{t}$ , (ii) 9.49 cm, (iii)  $2.40 \times 10^6 \text{ sec}$ , (iv)  $6.40 \times 10^6 \text{ days}$

### Convection

*Convection* is heat transfer due to macroscopic displacement of a fluid. The displacement can be spontaneous, as when steam carries heat away from a hot cup of tea - or forced, as done inside a refrigerator compressor.

For example, consider a pot of water initially at  $10^\circ\text{C}$  that sits on a kitchen stove burner maintained at  $110^\circ\text{C}$ .

1. Conduction: Heat is introduced to the liquid by contact with the bottom of its metal container, in contact with the heat source.
2. Convection cells: Fluid parcels nudge their way to the surface, spreading horizontally, and submerging when displaced by warmer fluid.
3. Turbulence: The bottom of the fluid becomes much warmer than the surface, and the convection cells burst into mushroom-cloud shapes.
4. Boiling: Discernible patterns vanish, and the fluid expels its heat by ejecting the most energetic particles.

5. Steam: Steam rapidly expands (if not constrained), doing work on the atmosphere.

Steps (2) through (5) each involve convection.

### Electromagnetic Radiation

*Electromagnetic radiation* is energy transfer that uses photons as a carrier. All objects continuously absorb and expel energy through photon exchange with the environment. The net rate of heat flow is given by Stefan's law,

$$\frac{dQ}{dt} = Ae\sigma (T_{\text{obj}}^4 - T_{\text{env}}^4) , \quad (3.11)$$

where  $A$  is the object's exposed surface area,  $e$  is the emissivity ( $0 \leq e \leq 1$ ) of the material, and  $\sigma$  is the *Stefan-Boltzmann* constant,  $5.67 \times 10^8 \text{ W m}^{-2} \text{ K}^{-4}$ . Note the temperature is counted in Kelvin units, which scales proportionally to the centigrade scale but equals zero at  $T = -273.15^\circ\text{C}$ .

A hot electric stove coil emits intense infrared radiation with wavelengths ranging from  $10^3 \text{ nm}$  to  $10^6 \text{ nm}$ . (Your skin easily detects these rays.) With increasing power, the range of emitted wavelengths widens, and eventually the coil visibly glows red with  $\lambda = 700 \text{ nm}$ . (Your eyes easily detect these.) With even more increasing power, the stove coil becomes 'white hot', emitting a very wide spectrum of wavelengths.

A hypothetical object useful for discussing radiation is the *blackbody*, which has  $e = 1$ , absorbing all incident radiation. Contrastly, a *reflector* absorbs no radiation.

#### Problem 12

Earth's upper atmosphere receives roughly  $1.50 \times 10^3 \text{ W/m}^2$  of energy from the sun by thermal radiation. The distance from the earth to the sun is  $1.50 \times 10^{11} \text{ m}$ , and the radius of the sun  $6.96 \times 10^8 \text{ m}$ . Use conservation of flux to calculate the surface temperature of the sun. Answer: About 6000 Kelvin.

#### Problem 13

*Wandering in the Desert:* Consider an unfortunate person walking at 5 km/h on a hot day in the desert, wearing only a bathing suit. The person's skin temperature tends to rise due to four mechanisms:

- Energy is generated by metabolic reactions in the body at a rate of 280 W, and almost all of this energy is converted to heat that flows to the skin.

- Heat is delivered to the skin by convection from the outside air at a rate equal to  $k'A_{\text{skin}}(T_{\text{air}} - T_{\text{skin}})$ , where  $k'$  is  $54 \text{ J/}^\circ\text{C m}^2\text{h}$ , the exposed skin area  $A_{\text{skin}}$  is  $1.5 \text{ m}^2$ , and the air temperature  $T_{\text{air}}$  is  $47^\circ\text{C}$ .
- The skin absorbs radiant energy from the sun at a rate of  $1400 \text{ W/m}^2$ .
- The skin absorbs radiant energy from the environment, which has temperature  $47^\circ\text{C}$ .

Assume the emissivity of the skin is  $e = 1$  and the skin temperature is  $36^\circ\text{C}$ . (i) Determine the net heat flow into the person due to the four mechanisms. (ii) At what rate (in liters per hour) must perspiration evaporate from the person's skin to maintain a constant skin temperature? (Assume sweat is made of water which has  $L_v = 2.42 \times 10^6 \text{ J/kg}$ .) (iii) Suppose instead that the person is protected by light colored clothing with  $e = 0$  such that the skin exposed is  $0.45 \text{ m}^2$ . (The convective heat exchange is not affected by the clothing.) What is the rate of perspiration now required? Answer: (i) 280 W, 0.248 W,  $2.10 \times 10^3 \text{ W}$ , 893 W, (ii) 4.87 L/h, (iii) 1.75 L/h

## 1.5 Atmospheric Qualities

### Vapor Pressure

The *vapor pressure* of a substance is the pressure at which the vapor phase is in equilibrium with the solid or liquid phase at a given temperature. For example, water and air in a sealed container will begin mixing by evaporation and condensation (of water molecules in and out of the air). Equilibrium is achieved when the partial pressure  $P_W$  of water *in the air* is equal to the vapor pressure  $P_0$ .

The following table maps out the vapor pressure of water as a function of temperature:

Temperature ( $^\circ\text{C}$ )	Vapor Pressure ( $\text{Pa} \times 10^3$ )
10	1.23
12	1.40
14	1.60
16	1.81
18	2.06
20	2.34
22	2.65
24	2.99
26	3.36
28	3.78
30	4.25
40	7.34

Note one Pascal (Pa) is equal to one Newton per square meter.

### Humidity

The *relative humidity* is defined as the ratio

$$H = \frac{P_W}{P_0},$$

always expressed as a percentage and never exceeding 100%. Because Earth's atmosphere is considered open instead of closed,  $H$  is typically much less than unity. On a rainy day,  $H$  becomes close to unity. In either case,  $P_0$  is much less than the atmospheric pressure  $P_A$ , which is near  $10^5$  Pa.

#### Problem 14

At  $24^\circ\text{C}$  and at 50.0% relative humidity, what is the partial pressure of water vapor in the atmosphere? Answer:  $P_W = 1.50 \times 10^3$  Pa

#### Problem 15

At  $24^\circ\text{C}$  and at 50.0% relative humidity, what is the mass density of the water vapor in the air? (Hint:  $M = 18 \times 10^{-3}$  kg/mol.) Answer:  $\rho = 0.0109$  kg/m<sup>3</sup>

### Dew Point

Consider an ice-cold glass sitting in a room. After a short time, water droplets form on the outside of the glass. To explain this, observe first that the air surrounding the glass, which itself contains water molecules, is cooled by conduction. The vapor pressure of the surrounding molecules therefore decreases (see table above), causing the relative humidity surrounding the glass to increase. When the relative humidity reaches 100%, the corresponding temperature is called the *dew point*, denoted  $T_{\text{dew}}$ .

At the dew point temperature, *further cooling cannot result in increased humidity*, which is already at unity, so the density of water molecules surrounding the glass must decrease. The excess molecules stick to the glass to form droplets. Note that the dew point is always less than the surrounding room temperature. The higher the relative humidity, the closer the dew point is to the ambient temperature.

#### Problem 16

Suppose the air temperature in a laboratory is  $24^\circ\text{C}$ , and a physics student cools a half-filled drink by adding ice. He finds that water begins to condense on the glass when its temperature reaches  $12^\circ\text{C}$ . What is the relative humidity in the room? Answer: 46.8%

### Clouds and Fog

Clouds and fog are easily explained in the terms defined above. Simply put, condensation (100% relative humidity) occurs at the altitude where the air temperature equals the dew point.

#### Problem 17

Consider a spring day when the air temperature on the ground is  $24^\circ\text{C}$  and the relative humidity is 50%. Assume that the partial pressure of water does not change with elevation, and that the air temperature decreases with altitude at a rate of  $0.06^\circ\text{C}/100\text{m}$ . (i) At what altitude will clouds form? (ii) If the relative humidity on the ground is higher, will the clouds form at a higher or lower altitude? (iii) If the temperature gradient is less, will the clouds form at higher or lower altitude? Answer: (i) 1833 m, (ii) lower, (iii) higher

## 1.6 Ideal Gas

The chain of discoveries leading to the understanding of gases spans across several centuries.

### Boyle's Law

In the seventeenth century, Robert Boyle (1627 - 1691) performed numerous studies on the properties of gases using the materials of his day (simple glassware and metals). The most famous fruit of his effort, called *Boyle's Law*, states that *the pressure of a fixed amount of gas maintained at constant temperature is inversely proportional to the volume of the gas*:

$$P \propto 1/V$$

### Charles's Law

A similar discovery about gases that came out of France in the 1780s, now known as *Charles's Law*, stating that *the volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature of the gas*:

$$V \propto T$$

### Lord William Kelvin

The linear relationship between volume  $V$  and temperature  $T$  found by Charles has an interesting feature that he probably didn't notice. All experimental data was indicating that any plot that displays  $V(T)$  for *any* substance at *any* pressure has an  $x$ -intercept at  $-273.15^\circ\text{C}$ . Scottish physicist Kelvin realized the significance of this in 1848, and seized the opportunity to name a new temperature scale after himself.

The *Kelvin temperature scale* resembles the centigrade system in every way with one exception: the bottom of the scale, 0 *Kelvin*, corresponds to  $-273.15^\circ\text{C}$ , also known as *absolute zero*. As it turns out, absolute zero is the limit low temperature for any object in the universe.

### Avogadro's Law

Italian scientist Amedeo Avogadro made his contribution in 1811, hypothesizing correctly that *the volume of a gas at constant temperature and pressure is proportional to the number of particles  $N$  composing the gas*:

$$V \propto N$$

### Ideal Gas Equation

Compiling the above achievements into a single equation of state, we arrive at the *ideal gas equation*:

$$PV = NK_B T \quad (3.12)$$

Equation (3.12) describes the macroscopic behavior of all  $N$  particles in a gas at pressure  $P$  and temperature  $T$  (in Kelvin) occupying volume  $V$ . The constant  $K_B$  is the *Boltzmann constant*, and has the experimental value  $1.381 \times 10^{-23} \text{ J/K}$ .

Sometimes in physics (and more often in chemistry) the quantity  $NK_B$  is written instead as  $nR$ , where  $n$  is the number of moles of the gas, and  $R$  is the *ideal gas constant*, measured as  $8.315 \text{ J mol}^{-1} \text{ K}^{-1}$  (Joules per mole-Kelvin).

### Ideal Gas Model

The ideal gas law is an approximate (but usually accurate) description of a realistic gas. As an equation of state, (3.12) holds if the following assumptions can be safely made:

- The volume of the container holding the gas is much greater than the total volume of the constituent gas particles.
- The separation between gas particles is much greater than the diameter of a given particle.
- A given particle's position and direction of travel (not its speed) is completely random.
- Particles do not interact among themselves, with the exception of perfectly elastic collisions.
- The container walls exchange momentum with the gas particles isotropically and don't deform.

- At a given instant,  $P$ ,  $V$ ,  $N$ , and  $T$  are uniform throughout the gas (quasistatic approximation).

Typically, the subscript  $B$  is typically dropped from the Boltzmann constant; thus we simply write  $K$  for now on.

### Problem 18

A rigid box of capacity  $0.5 \text{ m}^3$  is initially open, but is then sealed, trapping air inside at  $20^\circ\text{C}$  at atmospheric pressure. The box is then heated until the pressure inside becomes 3 times that of the atmosphere. Calculate the temperature of the trapped air (in Kelvin) after heating. How many particles are in the box? Answer:  $T = 879.45 \text{ K}$  and  $N = 1.25 \times 10^{25}$ .

## 2 Kinematic Gas Theory

Consider a sealed rigid vessel of volume  $V$  containing  $N$  non-interacting particles, not necessarily ideal gas. Such a gas has constant pressure and temperature at equilibrium.

### 2.1 Relative Velocity

Of all  $N$  particles in the gas, choose any two of them, where particle '1' has mass  $m_1$  and moves with velocity  $\mathbf{v}_1$ . Similar can be said for particle '2'. Borrowing from two-body analysis, we can write the kinetic energy of the pair as

$$T = \frac{1}{2} m^* v_{\text{rel}}^2 + \frac{1}{2} (m_1 + m_2) v_0^2,$$

where  $\mathbf{v}_0$  is the velocity of the center of mass,  $\mathbf{v}_{\text{rel}}$  is the relative velocity between the particles, and  $m^*$  is the reduced mass. If  $m_1$ ,  $m_2$  are equal to the same mass  $m$  then  $m^*$  reduces to  $m/2$ .

Starting with the relative velocity

$$\mathbf{v}_{\text{rel}} = \mathbf{v}_2 - \mathbf{v}_1,$$

square both sides and take the average of each term to write

$$\langle v_{\text{rel}} \rangle = \sqrt{\langle v_1 \rangle^2 + \langle v_2 \rangle^2 - 2 \langle \mathbf{v}_1 \cdot \mathbf{v}_2 \rangle}.$$

If we assume all particles are identical, then the averages  $\langle v_1 \rangle$ ,  $\langle v_2 \rangle$  are equal to the same velocity  $\langle v \rangle$ . Furthermore, we have that  $\langle \mathbf{v}_1 \cdot \mathbf{v}_2 \rangle$  resolves to zero, because all velocity vectors are random and uncorrelated. From this we conclude

$$\langle v_{\text{rel}} \rangle = \sqrt{2} \langle v \rangle,$$

which is to say the average relative velocity between each particle is about 1.41 times the average absolute velocity of the particles in the gas.

### Mean Free Path

Assuming a particle in the gas are spherical with radius  $r$ , the size of a the particle is characterized by the cross-sectional area  $\sigma$  given by

$$\sigma = \pi (2r)^2 .$$

In the time  $\Delta t$  between any two collisions, a particle carves out a Gaussian ‘tube’ of volume

$$V = \sigma \langle v_{\text{rel}} \rangle \Delta t ,$$

where  $\langle v_{\text{rel}} \rangle$  is the relative speed between the particle and its target (another particle).

We can also write the collision rate  $f = \Delta N / \Delta t$ . At the least,  $f$  is proportional to the density of the gas  $N/V$ , and is also proportional to the the product  $\sigma \langle v_{\text{rel}} \rangle$ . Thus we write

$$f = \frac{\Delta N}{\Delta t} = \sigma \langle v_{\text{rel}} \rangle \frac{N}{V} .$$

Borrowing from wave mechanics, a frequency  $f$  is associated with a wavelength  $\lambda$  by a velocity term:  $\lambda f = \langle v \rangle$ , and works out to be

$$\lambda = \frac{\langle v \rangle}{f} = \frac{\langle v \rangle}{\sigma \langle v_{\text{rel}} \rangle (N/V)} = \frac{1}{\sigma \sqrt{2}} \frac{V}{N} . \quad (3.13)$$

The distance  $\lambda$  is the *mean free path* for particles of radius  $r$  in the gas. Notice the inverse proportionality to the density and the cross-sectional area. The smaller the particles and the less dense they are, the longer they go before a collision.

#### Problem 19

Show that the mean free path for ideal gas molecules is

$$\lambda = \frac{1}{\sigma \sqrt{2}} \frac{KT}{P} .$$

## 2.2 Pressure

We advance on the kinematic gas problem by calculating the pressure in two not so very different ways. For a setup we continue considering a sealed container with volume  $V$  containing gas as temperature  $T$ . Starting from so little, the only freebie we get is that the particle number density is uniform and equal to  $N/V$ . Going forward we’ll refer to  $N/V$  as density, but remember there are no mass units involved.

### Heuristic Pressure Calculation

Inside the vessel, consider a cylindrical Gaussian cylinder of length  $L$ , held so the longitudinal  $z$ -axis is perpendicular and adjacent to the inner surface of the vessel with intersection area  $A$ , assumed circular. At any given instant, particles contained in the membrane are moving in all directions.

Question: How many of the particles  $\Delta N$  enclosed in the membrane will collide with the container wall in time interval  $\Delta t$ ? Answer: Statistically half of the enclosed particles collide with the wall (the other half are heading away). A particle will collide with the wall in a time interval  $\Delta t$  if it is heading toward the wall and within a distance  $L = |v_z| \cdot \Delta t$  of the wall, where  $v_x$  is the  $x$ -component particle’s absolute speed,  $\sqrt{\langle v^2 \rangle}$ . The collision rate is also proportional to the overall density of the gas,  $N/V$ . Therefore we may write

$$\Delta N = (1/2) (A |v_z| \Delta t) (N/V) .$$

On any collision with the container wall, there are two contributions to the momentum exchange: (i) the wall first absorbs momentum  $p_z$  to momentarily stop the gas particle, and (ii) the wall then imparts momentum  $-p_z$  to the particle, with a total exchange of  $\Delta p = 2mv_z$  per collision.

By the impulse-momentum theorem  $F dt = m dv$ , the definition of pressure gives

$$P = \frac{F}{A} = \Delta N \frac{1}{A} \frac{\Delta p}{\Delta t} ,$$

and after inserting what we know about  $\Delta N$  and  $\Delta p$ , we have

$$P = \frac{N}{V} m \langle v_z^2 \rangle .$$

Assuming the gas to be isotropic and living in three dimensions, it follows that

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_z^2 \rangle ,$$

bringing us to the result

$$P = \frac{1}{3} \frac{N}{V} m \langle v^2 \rangle . \quad (3.14)$$

#### Problem 20

In a 60 sec interval, 700 hailstones strike a  $0.5 \text{ m}^2$  glass window at an angle of  $45^\circ$  with respect to the normal to the window surface. Each hailstone has mass of 4.0 g and speed 8.0 m/s. If the collisions are purely elastic, Calculate the average force and pressure on the window.

### Formal Pressure Calculation

Inside the vessel, a given particle has any speed between zero and infinity in any direction. Introducing  $f(\mathbf{v})$  as a generalized velocity distribution, we write the normalization condition as

$$1 = \int_{\text{all } \mathbf{v}} f(\mathbf{v}) d^d v ,$$

where  $d$  is the number of dimensions in velocity space.

Performing the prior analysis using more vector language, the same Gaussian cylindrical membrane of length  $L$  inside the vessel touches the inner  $z$ -wall with common area element  $-dA\hat{\mathbf{z}}$ , where  $dA = dx dy$ . For particles with speed  $v$  inside the Gaussian cylinder, the length is represented by the vector  $\mathbf{L} = (dt)\mathbf{v}$ . The number of particles  $\Delta N$  destined to collide with the wall is proportional to the macroscopic density  $N/V$  times the volume  $d\mathbf{A} \cdot \mathbf{L} = dA dt v_z$ . Upon collision, the particle reverses the  $z$ -component of its momentum, with  $dp_z = 2p_z$ . Particles with negative  $p_z$  are heading away from the wall and don't collide.

Collecting these observations, write the 'pressure operator' as

$$[P_v] = \Delta N \frac{dF}{dA} = \Delta N \frac{dp_z/dt}{dA} = \frac{N}{V} v_z 2p_z ,$$

and the total pressure is given by

$$P = \int_{\mathbf{v}} [P_v] f(\mathbf{v}) d^3 v ,$$

expanding to:

$$P = \int_{v_x=-\infty}^{v_x=\infty} \int_{v_y=-\infty}^{v_y=\infty} \int_{v_z=0}^{v_z=\infty} \times \frac{N}{V} v_z 2p_z f(\mathbf{v}) dv_x dv_y dv_z$$

Note the careful choice of limits on the  $v_z$  variable: no particles are coming from outside the container.

Since  $f(\mathbf{v})$  is an even function by symmetry arguments, it does no harm to integrate over the interval  $-\infty < v_z < \infty$  and divide by a factor of 2. The integral simplifies to

$$P = \frac{N}{V} \int_{\mathbf{v}} (v_z p_z) f(\mathbf{v}) d^3 v = \frac{N}{V} \langle v_z p_z \rangle ,$$

where the statistical definition of average has been used. Finally, note again from symmetry that  $3 \langle v_z p_z \rangle = \langle vp \rangle$ , and the pressure takes a form reminiscent of Equation (3.14):

$$P = \frac{1}{3} \frac{N}{V} \langle vp \rangle$$

### 2.3 Effusion

*Effusion* takes place as gas particles are allowed to escape through a small aperture in the enclosing vessel. While the substance is losing particles, energy, and so on - we still work within the quasistatic approximation to gain insight into the phenomenon.

#### Effusion Rate

Let us calculate the rate  $R$  (measured in  $\text{s}^{-1}$ ) at which particles that strike a small patch of area  $A$  from inside the vessel. This is analogous to the pressure calculation, however now we ignore momentum exchange. For this, we begin with

$$R = \int_{\mathbf{v}} [R_v] f(\mathbf{v}) d^3 v$$

such that

$$[R_v] = A \frac{N}{V} v_z .$$

Expressed in 3D spherical coordinates, the effusion rate is

$$R = \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi/2} \int_{v=0}^{v=\infty} \times A \frac{N}{V} v \cos(\theta) f(\mathbf{v}) v^2 dv \sin(\theta) d\theta d\phi ,$$

where the  $z$ -axis is perpendicular to the container wall on the patch  $A$ . The gas exists only above the  $z = 0$  plane, as indicated by the choice of limits on the variable  $\theta$ . In this coordinate system, it follows that the normalization condition is

$$\int_0^\infty f(\mathbf{v}) 4\pi v^2 dv = 1 .$$

Using the statistical definition of average velocity, the instantaneous effusion rate simplifies down to

$$R = \frac{A}{4} \frac{N}{V} \langle v \rangle . \quad (3.15)$$

#### Effusion Energy

With the effusion rate known, it's possible to frame the calculation for the average energy per particle carried away by effusion. Begin with the definition of the average energy

$$\langle E \rangle = \int_{\mathbf{v}} [E_z] f(\mathbf{v}) d^3 v ,$$

and use

$$[E_z] = \left( \frac{1}{R} \right) \left( A \frac{N}{V} v_z \right) \left( \frac{mv_z^2}{2} \right) .$$



Note that the  $\theta$ -integral resolves via

$$\int_0^{\pi/2} \cos^3(\theta) \sin(\theta) d\theta = \frac{1}{4},$$

and simplify the  $\langle E \rangle$  expression to deduce

$$\langle E \rangle = \frac{m \langle v^3 \rangle}{4 \langle v \rangle}. \quad (3.16)$$

### Problem 21

Show that the average effusion energy per ideal gas particle is  $\langle E \rangle = KT$ . Explain why the total energy carried away per effused particle is  $2KT$ . Compare with  $3NKT/2$  to explain why the temperature of the vessel holding an effusing gas decreases so rapidly.

## 2.4 Maxwell Speed Distribution

Our recent calculations for pressure and effusion are generally applicable and have not assumed the ideal gas model. To gain traction on the ideal gas, we borrow from a more general study of Boltzmann factors to write the *Maxwell(-Boltzmann) speed distribution*:

$$D(v) dv = \left( \frac{m}{2\pi KT} \right)^{3/2} 4\pi v^2 e^{-mv^2/2KT} dv \quad (3.17)$$

The chance of finding an ideal gas particle with speed within the interval  $[v_1, v_2]$  equals the area under  $D(v)$  curve spanning that interval, or

$$P(v_1 < v < v_2) = \int_{v_1}^{v_2} D(v) dv.$$

The curve ‘opens up’ parabolically near speed  $v = 0$ , has a finite peak, and dies off exponentially for very large  $v$ .  $D(v)$  is already normalized such that  $P = 1$  for the interval  $[0, \infty]$ .

Note also there is one dependent variable in  $D(v)$ , but it is indeed a three-dimensional equation: the  $4\pi v^2$  term is byproduct of spherical coordinates in ‘velocity space’.

### Average Speed

With  $D(v)$  on hand, we use Gaussian integrals to calculate the average speed  $\langle v \rangle$  for the ideal gas:

$$v_{\text{ave}} = \langle v \rangle = \int_0^\infty v D(v) dv = \sqrt{\frac{8KT}{\pi m}} \quad (3.18)$$

### Problem 22

Use Gaussian integrals to prove the following:

$$\begin{aligned} \langle v^2 \rangle &= \frac{3KT}{m} \\ \langle v^3 \rangle &= \frac{4KT \langle v \rangle}{m} \\ \langle v^4 \rangle &= \frac{5KT \langle v^2 \rangle}{m} \end{aligned}$$

### Maximum Speed

A single derivative of Equation (3.17) determines the peak  $v_{\text{max}}$ :

$$v_{\text{max}} = \sqrt{\frac{2KT}{m}} \quad (3.19)$$

### RMS Speed

The *root mean square* speed is defined as  $\sqrt{\langle v^2 \rangle}$ , or

$$v_{\text{rms}} = \sqrt{\frac{3KT}{m}}. \quad (3.20)$$

Writing each result side-by-side, we see:

$$v_{\text{max}} < v_{\text{ave}} < v_{\text{rms}},$$

or

$$\sqrt{\frac{2KT}{m}} < \sqrt{\frac{8KT}{\pi m}} < \sqrt{\frac{3KT}{m}}$$

The numerical coefficients are approximately 1.414, 1.596, and 1.732 respectively.

### Problem 23

Ideal gas molecules in a container have the following measured speed distribution:

Speed (m/s)	Percentage
220	10%
250	10%
500	15%
650	30%
900	20%
1300	15%

Calculate the average speed, the rms speed, and the most probable speed. If the system is ideal gas of molecular mass  $M = 50 \times 10^{-3}$  kg/mol, what is the temperature? Answer: 690 m/s, 768 m/s, 650 m/s, 1180 K

### Problem 24

The escape speed for a particle to leave the gravitational influence of a massive body is given by  $(2GM/R)^{1/2}$ . The temperature near the top of Jupiter’s multicolored cloud layer is about 140K. The

temperature of Earth's atmosphere at 20 km is 220 K. Calculate the RMS speed of  $H_2$  molecules in each of those environments. Give the answer as a fraction of the escape speed from the respective planet. Answer: 14.7% for Earth and 2.16% for Jupiter, explaining the rarity of  $H_2$  in Earth's atmosphere. Jupiter's atmosphere consists of 89%  $H_2$  plus other gases.

### Problem 25

Ceres is an asteroid with a mass equal to 0.014 times the mass of the Moon, has density  $2400 \text{ kg/m}^3$ , and surface temperature around 200 K. Can this object support an  $O_2$  atmosphere? Answer:  $v_{\text{rms}}/v_{\text{esc}} = 72.9\%$  thus  $O_2$  will largely leave the asteroid.

## 2.5 Equipartition of Energy

### Internal Energy

Assuming gas particles do not mutually interact at a distance, the quantity  $m\langle v^2 \rangle/2$  represents the average internal energy per particle in the system. According to Equation (3.14), we find the general result

$$\langle U \rangle = \frac{m\langle v^2 \rangle}{2} = \frac{3PV}{2N},$$

or, scaling by all  $N$  particles,

$$U = \frac{3}{2}PV, \quad (3.21)$$

where for an ideal gas, the internal energy resolves to

$$U = \frac{3}{2}NKT.$$

Focusing on the factor of 3 momentarily, recall that it arises from symmetry by generalizing to three dimensions from one. Let us further generalize the idea of 'dimension' to mean 'degree of freedom'. That is, point-like gas particles in a box have three translational degrees of freedom. When molecules are *not* point-like, their motions may include rotation and vibration. These modes of motion (unavailable to points or spheres) make new contributions to the internal energy.

For an ideal gas comprised of non-point-like molecules, we will eventually prove the internal energy obeys

$$U = \frac{f}{2}NKT, \quad (3.22)$$

where  $f$  is the number of degrees of freedom available to a given molecule. Note that each degree of freedom must be *quadratic* with respect to its dependent variable. Kinetic energy is  $mv^2/2$ , and similarly rotational and vibrational energies are  $I\omega^2/2$  and  $k\Delta x^2/2$ , respectively.

### Problem 26

Insert the ideal gas Equation (3.12) into the internal energy Equation (3.21) to recover the formula for  $v_{\text{rms}}$ .

### Problem 27

The temperature of 7.00 mol of helium gas, considered ideal, is increased by 2.00 K. What is the change in internal energy?

### Equipartition Theorem

Equation (3.22) is a corollary of a more general statement called the *equipartition theorem*, stating:

*The internal energy per molecule gains a factor of  $KT/2$  for each independent quadratic degree of freedom.*

This theorem can be *derived* in full generality using statistical mechanics (also accounting for non-quadratic potentials), but is beyond the scope of this study.

### Diatomic Molecules

Consider a generalized ideal gas made of  $N$  dumbbell-shaped  $H_2$  molecules. In accordance with (3.22), we count the quadratic degrees of freedom per molecule as follows:

- Three translational modes, so  $f$  is at least 3.
- Two degrees of rotational freedom. The diatomic molecule may spin like a baton in two orthogonal modes, however rotations about the axis joining the atoms do not change during collision. So far,  $f = 3 + 2$ .
- Two contributions from the single vibrational mode (a combination of both kinetic and potential energies), increasing  $f$  again by 2.

We expect therefore that the energy of a diatomic gas is

$$U_{\text{dia}} = (7/2)NKT.$$

However,  $f = 7$  is only observed at high temperatures. Experiments performed on  $H_2$  gas have shown that only translational modes occur at temperatures under 200 K. Below this, the rotational and vibrational energies are 'frozen out' and don't contribute to the internal energy. By 400 K, the two rotational modes are fully active. Vibrational modes finally show themselves around 4000 K. Evidently, diatomic molecules have  $f$  appearing as 3, 5, or 7, depending on  $T$ .

Problem 28

Use the equipartition theorem to find the total rotational energy of the molecules in 4.00 mol of diatomic gas at 310 K.

**2.6 Heat Capacity**

The heat capacity is the factor that couples energy change to temperature change for a given substance (not news):

$$C = \frac{dQ}{dT} \quad (3.23)$$

It is generally wrong to assume that *all* added energy contributes to the kinetic energy of the gas, as some effort is ‘wasted’ on volume expansion of the system. We therefore frame heat capacity calculations somewhere between two extremes: constant volume and constant pressure, where  $C$  gains a respective  $V$ - or a  $P$ -subscript.

**Ideal Gas at Constant Volume**

Consider a sample of ideal gas inside a sealed, infinitely rigid container of fixed volume  $V$ . It follows that all added heat contributes to the kinetic energy, as only the pressure and temperature are variable. Using equations (3.22) and (3.23), we find

$$C_V = \frac{f}{2}NK. \quad (3.24)$$

For one mole of monatomic gas with point-like constituents with  $f = 3$  (such as helium or argon), the prediction for  $C_V$  evaluates to

$$C_{V_{\text{mon}}} = \frac{3}{2}R = 12.47 \frac{\text{J}}{\text{mol} \cdot \text{K}},$$

in very good agreement with experiments. Due to complications that are later solved by quantum mechanics, Equation (3.24) is only accurate for some gases.

**Ideal Gas at Constant Pressure**

For systems allowed to change volume while maintained at constant pressure, the added energy  $\Delta Q$  splits according to

$$\Delta Q = \Delta U_{\text{int}} + P\Delta V,$$

where the increase in translational, rotational, and vibrational motions of the molecules is all contained in  $\Delta U_{\text{int}}$ , and  $P\Delta V$  is the energy needed to shove the environment out of the way as the gas expands. Taking a  $T$ -derivative of the above yields

$$C_P = C_V + NK, \quad (3.25)$$

where  $P\Delta V/\Delta T$  has been replaced using the ideal gas equation.

**Gamma Factor**

The dimensionless ratio  $C_P/C_V$  is called the *gamma factor*, which comes out to

$$\gamma = \frac{C_P}{C_V} = 1 + \frac{2}{f}. \quad (3.26)$$

Problem 29

Methane ( $\text{CH}_4$ ) is a 3-dimensional molecule - a tetrahedron with carbon in the center. Determine the best approximations for  $C_V$  and  $\gamma$ . Answer:  $24.9 \text{ J mol}^{-1}\text{K}^{-1}$  and 1.33

**Elemental Solids**

The equipartition theorem allows easy calculation of the heat capacity of many solids. For our purposes, a solid is regarded as a semi-frozen ideal gas, which we take as a periodic arrangement of molecules with no contributions to thermal energy from translational or rotational motions. The structure is held together by quadratic potentials, thus such solids have six degrees of freedom per molecule: three components of kinetic energy due to vibration and three corresponding quadratic potentials.

According to (3.24), one mole of ‘frozen gas’ with  $f = 6$  has

$$C_{V_{\text{solids}}} = \frac{6}{2}R = 24.9 \frac{\text{J}}{\text{mol} \cdot \text{K}},$$

which is obeyed by *all* elemental solids at high enough temperature, known as the *rule of Dulong and Petit*.

**2.7 Van der Waals Model**

The *van der Waals* model is an extension of the ideal gas law that accounts for the particle size and the interactions between particles. To write a generalized ideal gas law, two experimental constants enter the mix - blandly named  $a$  and  $b$ .

The starting point is the ideal gas model, with equation of state  $PV = NKT$ . Supposing each of  $N$  particles in a sample (gas or liquid) has volume  $b$ , we make the replacement

$$V \rightarrow V - Nb,$$

where the variable  $V$  is understood as the volume available for the sample to occupy. The particles themselves do not contribute to  $V$ .

Next we assume particles interact through the attractive *Leonnard Jones potential*. Without increasing temperature, particle interactions lead to an increase in number density  $N/V$  and pressure  $P$ , as evident by considering a particle on the surface layer of the sample. On the surface layer, the net force on a particle is inward, proportional in strength to  $N/V$ . The total force inward is proportional to the surface area of  $V$ , contributing another factor  $N/V$ . It follows that the correction to pressure is

$$P \rightarrow P + a(N/V)^2,$$

where  $a$  is a constant of dimension  $\text{kg m}^5 \text{s}^{-2}$ .

The van der Waals equation is

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NKT, \quad (3.27)$$

and is accurate for many types of gases and fluids. Water vapor has  $a = 0.5507 \text{ J m}^3 \text{mol}^{-2}$  and  $b = 3.04 \times 10^{-5} \text{ m}^3/\text{mol}$ . In the same units,  $N_2$  gas has  $a = 0.1361$  and  $b = 3.85 \times 10^{-5}$ , and  $H_2$  gas has  $a = 0.0247$  and  $b = 2.65 \times 10^{-5}$ .

## 3 First Law

### 3.1 First Law of Thermodynamics

Thermodynamic systems are subject to energy conservation as any other mechanical system would. If  $U$  is the internal energy of a substance at pressure  $P$  and volume  $V$ , any thermal energy  $dQ$  added (or removed) must follow

$$dU = dQ - PdV, \quad (3.28)$$

known as the *first law of thermodynamics*.

To make sense of the sign of the  $PdV$  term, imagine adding heat  $+dQ$  to a gas sample using a candle. If the experiment is prepared such that the temperature does not change, making  $dU = 0$ , then the gas necessarily expands its volume. The  $PdV$  term must appear negative to balance out  $dQ$ .

### 3.2 Thermodynamic Processes

A *thermodynamic process* is any change in the state variables characterizing a thermodynamic system. In many cases, only some variables may change, such as temperature and pressure, while other variables remain fixed, such as volume and number of particles. In the following we classify some of the common thermodynamic processes.

#### Isothermal Process

An *isothermal* process is one that leaves the system's temperature unchanged, which generally means there is no change in the system's internal energy. The first law with  $dU = 0$  reads  $0 = dQ - PdV$ .

#### Isochoric Process

A process that leaves the system's volume unchanged (easier said than done) is classified as *isochoric*. The  $dV$  term in the first law is zero by construction, so all heat added to the system contributes to internal energy via  $dU = dQ - 0$ .

#### Isobaric Process

A process that leaves the system's pressure unchanged (easily said and easily done) is classified as *isobaric*. For example, the macroscopic work done on a gas is not an integral  $\int PdV$ , but simply the product  $P\Delta V$ .

#### Adiabatic Process

*Adiabatic* processes are those that have zero net heat transfer into or out of the system. The first law of thermodynamics quantifies this by  $dU = 0 - PdV$ , where any internal energy change  $dU$  is balanced out by response in pressure and volume.

#### Reversible Processes

Many processes in classical mechanics (oscillations, orbits, etc.) are *reversible*, where the system may backtrack along its path in configuration space by reversing time  $t \rightarrow -t$  without violating any laws of physics or probabilistic expectations. Only *some* thermodynamic processes are reversible, and only if conditions are right, with one example being isothermal phase change between water and ice at  $0^\circ\text{C}$  in a sealed container.

In reality, thermodynamic phenomena are naturally *irreversible*, such as when a bomb explodes, or when scrambling an egg. Witnessing either of these in reverse would be extremely unlikely. To restore such a system to its original state, an external reorganizing force would have to intervene.

### 3.3 Ideal Gas Processes

We now examine the consequences of thermodynamic processes for a controlled sample of ideal gas, always obeying the ideal gas Equation (3.12).

**Isothermal**

For isothermal expansion in ideal gas, the total energy entering the gas equals the total work done on the environment, given by the integral

$$W = \int P dV = \int_{V_i}^{V_f} \frac{NKT}{V} dV ,$$

simplifying to

$$W = NKT \ln \left( \frac{V_f}{V_i} \right) . \quad (3.29)$$

That is, all added heat contributes to volume expansion.

**Isochoric**

An isochoric process permits no volume change, which we studied when writing the heat capacity of ideal gas at constant volume. The first law tells us  $dQ = dU$ , where meanwhile we know  $dQ/dT = C_V = fNK/2$ . It follows that the work done during an isochoric process is

$$W = C_V \Delta T = \frac{f}{2} NKT \Delta T . \quad (3.30)$$

**Isobaric**

For an ideal gas, we found  $C_P = C_V + NK$ , leading to

$$W = C_P \Delta T = \left( \frac{f}{2} + 1 \right) NKT \Delta T . \quad (3.31)$$

**Adiabatic**

An adiabatic process usually involves a rapid expansion or compression of a gas that is ‘too fast’ for external heat transfer, making  $dQ = 0 = dQ - PdV$ . Inserting the ideal gas internal energy relation (3.22) into the first law, we write a differential equation

$$\frac{f}{2} dT = -T \frac{dV}{V} , \quad (3.32)$$

implying:

$$\begin{aligned} PV^\gamma &= \text{constant} \\ TV^{\gamma-1} &= \text{konstant} \end{aligned} \quad (3.33)$$

**Problem 30**

For a purely kinetic ideal gas, show that  $VU^{3/2}$  is constant.

The work entering an ideal gas during an adiabatic process is

$$W = \int P dV = NK \int \frac{T}{V} dV = NK \frac{f}{2} (T_i - T_f) ,$$

simplifying to

$$W = -\frac{PV}{T} \frac{f}{2} \Delta T . \quad (3.34)$$

Note the term  $(PV/T)$  may be evaluated at *any* point during the adiabatic process, so long as the combination of  $P$ ,  $V$ , and  $T$  are known simultaneously. Using relation (3.26), we may alternatively write

$$W = \frac{1}{1-\gamma} (V_f P_f - V_i P_i) . \quad (3.35)$$

The variable  $\gamma$  is always  $> 1$  by construction, thus (3.35) has a buried negative sign. If the *overall* sign of  $W$  is positive, the work is done *by* the gas. If negative, the work is done *on* the gas.

**Free Expansion of Ideal Gas**

Consider a sealed, perfectly-insulating vessel with ideal gas contained within half of its total volume. The other half of the vessel is vacuum, and a thin membrane separates the two compartments. The membrane is then punctured and the gas is allowed to freely expand into the vacuum until the two compartments are in equilibrium. (The system is not quasistatic during expansion.)

Such free expansion is an adiabatic process, as no heat enters or leaves the vessel through the insulated walls. The system does zero work, as no force is required to expand into vacuum. The temperature change is zero according to Equation (3.34), thus the internal energy change is also zero. In summary, we see

$$Q = W = \Delta T = \Delta U = 0 ,$$

showing the energy state of the gas is unchanged. Of course, the gas will never accidentally find itself crammed into one side of the box again; work *would* be required to compress the system to its original state. Free expansion of ideal gas is therefore irreversible.

**Problem 31**

Take a  $P$ -derivative of Equation (3.33) to derive

$$\frac{dT}{dP} = \frac{2}{f+2} \frac{T}{P} . \quad (3.36)$$

**Problem 32**

Consider an ideal gas of  $N$  particles with initial temperature  $T_i$  and initial volume  $V_i$  that is compressed to final volume  $V_f$ . Which process requires

more energy compress the gas, isothermal or adiabatic?

### Problem 33

At height  $z$  in the Earth's atmosphere, (i) show that a horizontal thin layer of air with (massless) volume density  $\rho(z)$  and pressure  $P(z)$  obeys the equation  $dP/dz = -mg\rho(z)$  at mechanical equilibrium, where  $m$  is the average mass of molecules in the air. (ii) Consider a bubble of gas that moves upward fast by expanding or shrinking adiabatically. Show that the temperature gradient experienced by the bubble is given by

$$\frac{dT}{dz} = -mg\rho(z) \frac{2}{f+2} \frac{T}{P}.$$

(iii) At low altitudes above sea level, the pressure decreases by about 1.2 kPa for every 100 m. For higher altitudes within the troposphere, show that

$$P(z) = P_0 e^{-mgz/KT_0},$$

where  $P_0$  and  $T_0$  are measured at sea level ( $P_0 \approx 101325$  Pa,  $T_0 \approx 288.15$  K).

### Problem 34

A scuba diver is swimming a depth of 25 m where the pressure is 3.5 atm. The air she exhales forms bubbles 8.0 mm in radius, which rise to the surface where the pressure is 1 atm. Assume the bubbles remain at the uniform 300 K temperature of the surrounding water. How much work is done by each bubble as it expands to the rising surface? Answer: 0.953 J

### Problem 35

When a quantity of monatomic ideal gas expands at a constant pressure of  $4.00 \times 10^4$  Pa, the volume of the gas increases from  $2.00 \times 10^{-3} \text{ m}^3$  to  $8.00 \times 10^{-3} \text{ m}^3$ . (i) What is the change in internal energy of the gas? (ii) Does heat flow into out of the gas? (iii) What is the magnitude of the heat flow? Answer: 360 J, 600 J into the gas.

## 3.4 Thermodynamic Cycles

A *thermodynamic cycle* is a chain of processes that bring an open system's state variables to a previous configuration. It follows that the net internal energy change  $\Delta U$  is zero for a complete thermodynamic cycle, meaning that any heat added to a system must be removed somewhere in the same cycle.

During any infinitesimal volume change, work done is equal to  $PdV$ . Integrated over a thermodynamic cycle, the total work done equals the area

enclosed by the loop on the  $PV$  diagram. If the loop traces out in a clockwise direction, the work output of the system is positive. When going counter-clockwise, the system absorbs work over a complete cycle.

### Heat Engine

A *heat engine* is a device that utilizes a thermodynamic cycle in repetition to perform 'useful' work. The *efficiency* of a heat engine is defined as the ratio of output work over input heat energy. Using the first law we write

$$e = \frac{W}{Q_H} = \frac{Q - \Delta U}{Q_H} = \frac{Q}{Q_H}. \quad (3.37)$$

Through a complete thermodynamic cycle, the net heat flow  $Q$  equals  $Q_H + Q_C$ . The efficiency is therefore

$$e = \frac{Q_H + Q_C}{Q_H} = 1 - \left| \frac{Q_C}{Q_H} \right|,$$

using the fact that  $Q_C$  is negative for a typical heat engine.

### Problem 36

Two moles of an ideal diatomic gas are taken around the cycle  $abc$  as shown in Figure 3.4. Data:  $P_a = 1.00 \times 10^5$  Pa,  $P_c = 1.40 \times 10^5$  Pa,  $V_a = 0.049 \text{ m}^3$ . If the path from  $b$  to  $c$  is isothermal, calculate the work done by the gas. Answer:  $-2300$  J

### Problem 37

Two moles of an ideal diatomic gas are taken around the cycle  $abc$  as shown in Figure 3.4. Data:  $P_a = 1.00 \times 10^5$  Pa,  $P_c = 1.40 \times 10^5$  Pa,  $V_a = 0.100 \text{ m}^3$ . If the path from  $b$  to  $c$  is adiabatic, calculate the volume of the gas at point  $c$ . Answer:  $0.13 \text{ m}^3$

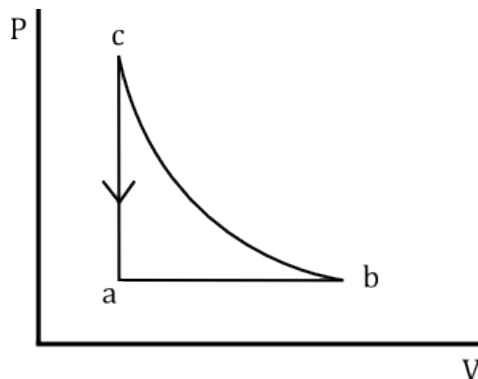


Figure 3.4:  $PV$  diagram showing thermodynamic cycle.

### Problem 38

A cylinder with a piston contains 0.150 mol of nitrogen at  $1.80 \times 10^5$  Pa at 300 K. The nitrogen may be treated as an ideal diatomic gas whose molecules can rotate, but not vibrate. The gas is first compressed isobarically to half its original volume. It then expands adiabatically back to its original volume, and is finally heated isochorically to its original pressure. (i) Do the arrows on the corresponding  $PV$  diagram point clockwise or counterclockwise? Draw it. (ii) Compute the temperatures at the beginning and end of the adiabatic expansion. (iii) Compute the minimum pressure. (iv) Compute the work done by nitrogen during one thermodynamic cycle. Answer: (i) counterclockwise, (ii) 150 K, 114 K, (iii)  $6.82 \times 10^4$  Pa, (iv)  $-75$  J

### Otto Cycle

Many automobiles operate on the gasoline-burning *Otto cycle*. Inside Otto engines, a fuel-air mixture (approximately ideal gas) is compressed inside a piston and then ignited with a spark, resulting in rapid volume expansion to ‘blast’ the piston outward, applying work that ultimately reaches the wheels. The spent fuel-air mixture is ejected from the piston and the process repeats. Engines in general have a different number of steps required to complete their thermodynamic cycles, with popular conventions being ‘two-stroke’ and ‘four-stroke’.

The Otto cycle consists of four thermodynamic processes illustrated in Figure 3.5. We begin analyzing an Otto engine piston as it is fully expanded at volume  $V_{\max}$  and filled with a fuel-air mixture (approximately ideal gas), ready to ignite. In this ‘cool’ state, the piston has temperature  $T_0$  pressure  $P_0$ .

1. Compression stroke (adiabatic): An external force (work left over from a previous cycle) rapidly compresses the piston to volume  $V_{\min}$ . The pressure of the fuel-air mixture thereby increases to  $P_1$ , and the temperature increases to  $T_1$ . Because no significant heat is added to the cylinder during the compression stroke, it is an adiabatic process.
2. Fuel ignition (isochoric): With the piston fully compressed, a spark ignites the fuel-air mixture, quickly releasing a great deal of kinetic energy  $Q_H$  into the gas. The pressure jumps quickly to  $P_2$ , and likewise the temperature to  $T_2$ . The volume remains constant at  $V_{\min}$ . The energy added follows the relation:

$$Q_H = nC_V (T_2 - T_1) ,$$

where  $n$  is the number of moles of fuel-air mixture in the piston.

3. Power stroke (adiabatic): The cylinder’s volume expands to  $V_{\max}$  following ignition, and whatever device is attached to the moving part of the piston receives organized work  $W$  (driving the car forward, for instance). The pressure drops to  $P_+$  during this process, but not quite down to  $P_0$ . The spent fuel-air mixture is still ‘hot’ at this point, having temperature  $T_+$ , slightly greater than  $T_0$ .
4. Exhaust stroke (isochoric): The cylinder expels the spent fuel-air mixture of energy  $Q_C$  to the environment and takes in a new fuel-air packet, returning the pressure to  $P_0$ . The piston effectively remains at  $V_{\max}$  (after intake of new fuel), and is ready again for a compression stroke. The (negative) energy added follows the relation

$$Q_C = nC_V (T_0 - T_+) .$$

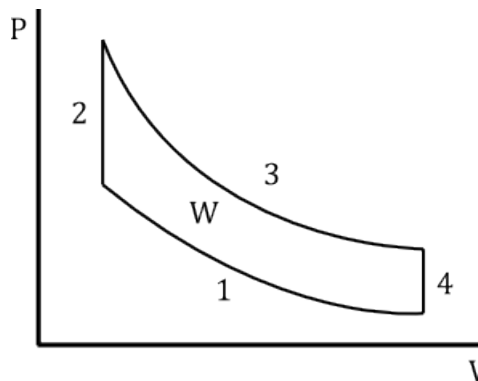


Figure 3.5: Otto cycle.

The efficiency of the Otto engine is straightforward to calculate by Equation (3.37), giving

$$e = 1 + \frac{Q_C}{Q_H} = 1 + \frac{T_0 - T_+}{T_2 - T_1} ,$$

but we can do better. The Otto cycle’s two adiabatic transitions obeys Equation (3.33), allowing all  $T$ -variables to cancel. Meanwhile, define the piston *compression ratio*  $r = V_{\max}/V_{\min}$  so the formula for  $e$  boils down to

$$e = 1 - \frac{1}{r^{\gamma-1}} . \quad (3.38)$$

#### Problem 39

How much of  $Q_C$  may be used to bolster to the power stroke of an engine? Answer: None, not even theoretically.

#### Problem 40

A gasoline engine takes in  $8.00 \times 10^3 \text{ J}$  of heat and delivers  $1.60 \times 10^3 \text{ J}$  of work per cycle. The heat is obtained from gasoline with a heat combustion of  $4.6 \times 10^4 \text{ J/g}$ . (i) What is thermal efficiency? (ii) How much heat is discarded in each cycle? (iii) What mass of fuel is burned in each cycle? (iv) If the engine goes through 70.0 cycles per second, what is the power output in watts? (v) What is the power in horsepower? Answer: 0.212,  $6.70 \times 10^3 \text{ J}$ ,  $1.85 \times 10^{-4} \text{ kg}$ ,  $1.62 \times 10^5 \text{ W}$ , 217 hp.

#### Problem 41

A Toyota Celica GT has a four cylinder Otto-cycle engine with a compression ratio of  $r = 9.50$ . The diameter of each cylinder, called the *bore* of the engine is 87.1 mm. The distance that the piston moves during the compression, called the *stroke* of the engine is 90.9 mm. The initial (and minimal) pressure of the air - fuel mixture (when the volume is maximal) is  $8.50 \times 10^4 \text{ Pa}$ , and the initial temperature is 300 K (same as the environment). Assume that 200J of heat is added to each cylinder in each cycle by burning the fuel (gasoline), which has  $C_V = 20.5 \text{ Jmol}^{-1}\text{K}^{-1}$  and  $\gamma = 1.40$ . (i) Calculate the work done in each cycle. (ii) Calculate the thermal energy released when the gas is cooled to the temperature of the outside air. (iii) Calculate the minimal volume of the air - fuel mixture. (iv) Calculate  $P$ ,  $V$ , and  $T$  just before ignition. Answer: 119 J, 81.3 J,  $6.05 \times 10^{-4} \text{ m}^3$ ,  $1.99 \times 10^6 \text{ Pa}$ ,  $6.37 \times 10^{-5} \text{ m}^3$ , 738 K

#### Diesel Cycle

Some automobiles and nearly all road shipping vehicles (excluding hybrid drives) operate on the *diesel cycle*. Like the Otto cycle, the diesel cycle entails four thermodynamic processes. Inside a diesel engine piston however, fuel-air mixture (approximated as ideal gas) is compressed until it self-ignites without the help of a spark, causing the power stroke. The ignition takes place in a constant-pressure condition, and the volume jumps almost instantly, much unlike the Otto cycle's ignition scenario.

#### Problem 42

Figure 3.6 is the  $PV$  diagram for the diesel cycle. The compression stroke, the instant of fuel ignition, power stroke, and exhaust stroke are labeled 1, 2, 3, 4, respectively. Assuming steps 1 and 3 are adiabatic, show that the efficiency of the diesel engine is given by

$$e = 1 - \frac{1}{\gamma} \frac{(c/b)^{-\gamma} - (c/a)^{-\gamma}}{(c/b)^{-1} - (c/a)^{-1}},$$

where volumes  $a$ ,  $b$ , and  $c$  are indicated on the horizontal axis and  $\gamma$  is the ratio  $C_P/C_V$ .

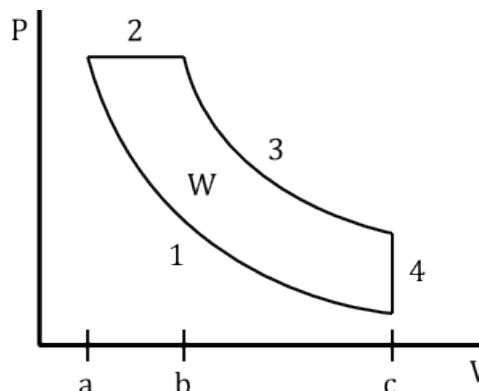


Figure 3.6: Diesel cycle.

#### Refrigerators

A refrigerator operates as a heat engine in reverse: work is required to displace heat from the cold reservoir to the hot reservoir. The working substance that circulates inside a refrigerator is a fixed amount of water, freon, or ammonia (no chemical exhaust). The operation is outlined as follows:

1. Starting in the gaseous phase, the working substance is forced through a compressor, emerging with reduced volume and increased temperature and pressure.
2. The substance goes through a long heat-conducting tube called the *condenser*, which is in thermal contact with the environment (hence the refrigerator needs to ventilate). In the condenser, the working substance loses heat  $Q_H < 0$  and changes phase to liquid.
3. The working substance then encounters a very small 'bottleneck' called the *throttle* that hinders most of the circulation. On the input side of the throttle, the temperature and pressure of the working substance are relatively high. The output side is at much lower temperature and pressure.
4. As a cold liquid, the working substance passes through the refrigerator body, warming again to the gaseous phase, absorbing energy  $Q_C > 0$ .

Like the heat engine, the refrigerator obeys the first law

$$Q_H + Q_C = Q_{in} = \Delta U + W,$$



where  $\Delta U = 0$  and  $W < 0$ . The merit of a refrigerator is not its efficiency, but instead the *coefficient of performance*, defined as the ratio of heat removed from the refrigerator body over the work required to do so. That is,

$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|}. \quad (3.39)$$

#### Problem 43

An ideal air conditioner takes heat from a room at 68.5°F and transfers it to the environment, which is at 93.1°F. For each joule of electrical energy required to operate the air conditioner, how many joules of thermal energy are removed from the room?

#### Problem 44

Liquid refrigerant at a pressure of  $1.34 \times 10^5$  Pa leaves the expansion valve of a refrigerator at  $-22^\circ\text{C}$ . It then flows through the vaporization coils inside the refrigerator and leaves as vapor at the same pressure at a temperature of  $-18^\circ\text{C}$ , the same temperature as the inside of the refrigerator. The boiling point of the refrigerant at this pressure is  $-18^\circ\text{C}$ , the heat of vaporization is  $1.60 \times 10^5$  J/kg, and the specific heat capacity of the vapor is  $485 \text{ J kg}^{-1} \text{ K}^{-1}$ . The coefficient of performance of the refrigerator is  $K = 2.52$ . If 8.00 kg of refrigerant flows through the refrigerator each hour, find the electric power that must be supplied to the refrigerator. Answer: 123 W

#### Problem 45

A heat pump designed for southern climates extracts heat from the outside air, and delivers air at  $20^\circ\text{C}$  to the inside of the house. Compute the coefficient of performance of the heat pump (i) in the south, where the outside temperature is  $5^\circ\text{C}$ ; (ii) in the north, where the outside temperature is  $-10^\circ\text{C}$ . (iii) Two identical houses, one in the north and one in the south, are heated by this pump, and maintain temperatures of  $20^\circ\text{C}$ . Considering heat loss through the walls, windows, and roof, what is the ratio of the electrical power required to heat the two houses? Answer: (i) 18.5, (ii) 8.77, (iii) 4.0

### Carnot Cycle

Sadi Carnot (1796-1832) designed an engine with maximal efficiency by using only reversible isothermal and reversible adiabatic processes. All heat transfer during the Carnot cycle occurs on isotherms; there is no heat transfer across finite temperature differences. No machine using the Carnot cycle would be ‘fast’ enough for industrial standards, but Carnot engines are still the most efficient type.

The gaseous working substance within a Carnot engine piston never leaves the piston, and undergoes no chemical change. Carnot engines rely on a literal ‘hot’ reservoir from which to draw energy, and a similar ‘cold’ reservoir to deposit energy. These two reservoirs may in practice be as simple as hot and cold containers of water. The four stages of the Carnot cycle go as follows:

1. Slow isothermal: A piston in the ‘compressed’ state enclosing a gas of volume  $V_{\min}$  is attached to a reservoir at high temperature  $T_H$  and absorbs heat  $Q_H$  isothermally. The volume swells to  $V_1$ , and the reservoir is removed. Recall from Equation (3.29) that

$$Q_H = NKT_H \ln \left( \frac{V_1}{V_{\min}} \right).$$

2. Fast adiabatic: The gas expands adiabatically, lowering its temperature from  $T_H$  until it reaches  $T_C$ . The volume swells once more to reach a maximum  $V_{\max}$ .
3. Slow isothermal: The system moves to contact the cold reservoir of temperature  $T_C$ , where isothermal compression takes the volume to  $V_2$  (with  $V_2 < V_1$ ). The discarded energy is

$$Q_C = -NKT_C \ln \left( \frac{V_{\max}}{V_2} \right).$$

4. Fast adiabatic: The system moves away from the cold reservoir and the gas is compressed adiabatically, raising its temperature from  $T_C$  until it reaches  $T_H$ . The volume returns to  $V_{\min}$ .

The efficiency of the Carnot engine, according to definition (3.37), is

$$e = \frac{Q_H + Q_C}{Q_H} = 1 - \frac{T_C \ln(V_{\max}/V_2)}{T_H \ln(V_1/V_{\min})},$$

where Equation (3.33) for adiabatic processes tells us  $V_{\max}/V_2 = V_1/V_{\min}$ , and thus

$$\frac{Q_C}{Q_H} = -\frac{T_C}{T_H}. \quad (3.40)$$

Astonishingly, the efficiency depends on neither the construction of an engine nor the properties of the working substance, only the reservoir temperatures:

$$e = 1 - \frac{T_C}{T_H} \quad (3.41)$$

#### Problem 46

Consider a Carnot engine operating between temperatures  $T_H$  and  $T_C$ , where  $T_C$  is above the ambient

temperature  $T_0$ . A second engine operates between the temperatures  $T_C$  and  $T_0$ . Show that the overall efficiency of this system is equal to the efficiency of a single Carnot engine operating between  $T_H$  and  $T_0$ .

#### Problem 47

A Carnot engine operating between two thermal reservoirs has an efficiency of  $e$ . When it is run in reverse, it becomes a Carnot refrigerator. Calculate the coefficient of performance. Answer:  $(1 - e)/e$

### Reversible Loops

By riding isothermal and adiabatic curves, Carnot successfully identified a closed loop in the  $PV$  diagram that is entirely reversible. It should follow that we may consider any reversible path as a stack of Carnot cycles. To capture this idea, write Equation (3.40) in the form

$$\frac{Q_C}{T_C} + \frac{Q_H}{T_H} = 0$$

where a path made of many isothermal and adiabatic segments must obey

$$\sum \frac{Q}{T} = 0.$$

Heat transfer on shared isotherms cancel, and the sum refers only to the boundary of the  $PV$ -curve. Taking a finer resolution, the sum generalizes to a path integral

$$\oint \frac{dQ}{T} = 0. \quad (3.42)$$

Evidently, there is *something* that links quantity  $dQ/T$  to the reversibility of thermodynamic processes.

## 4 Second Law

### 4.1 Entropy

The *entropy* of system is a quantity representing its ‘reversibility’. First surfacing in Equation (3.42), let us define the entropy as

$$S = \int \frac{dQ}{T}. \quad (3.43)$$

For reversible processes, the entropy can be found by direct integration of the above. For two states linked by an irreversible process, it suffices to calculate the entropy over some other path (in the  $PV$  diagram) consisting of reversible process that would connect those two states.

Adding to our list of terms for thermodynamic processes, any process that is both adiabatic and quasistatic is called *isentropic*, which means there is no entropy change in the process.

#### Problem 48

When 1.00 kg of water at 0°C is frozen to make ice, what is the entropy change? Answer:  $-1200 \text{ J/K}$

#### Problem 49

An object of mass  $m_1$ , specific heat  $c_1$ , and temperature  $T_1$  is placed in contact with a second object mass  $m_2$ , specific heat  $c_2$ , and temperature  $T_2 > T_1$ . As a result, object 1 heats to temperature  $T$  and object 2 cools to  $T'$ . (i) Show that energy conservation requires that  $m_1 c_1 (T - T_1) = m_2 c_2 (T_2 - T')$ . (ii) Show that the entropy increase of the system is

$$\Delta S = m_1 c_1 \ln(T/T_1) + m_2 c_2 \ln(T'/T_2).$$

### Isothermal Expansion of Ideal Gas

For isothermal expansion of ideal gas, we wrote the energy entering the system as Equation (3.29), implying  $\Delta Q = NKT \ln(V_f/V_i)$ . By the definition of entropy, it follows that

$$S = NK \ln \left( \frac{V_f}{V_i} \right). \quad (3.44)$$

### Isochoric Expansion of Ideal Gas

For isochoric expansion of ideal gas, we wrote the energy entering the system as Equation (3.30), implying  $dQ/dT = C_V$ . By the definition of entropy, it follows that

$$S = \int \frac{dQ}{dT} \frac{dT}{T} = C_V \ln \left( \frac{T_f}{T_i} \right). \quad (3.45)$$

### Isobaric Expansion of Ideal Gas

For isobaric expansion of ideal gas, we wrote the energy entering the system as Equation (3.31), implying  $dQ/dT = C_P$ . By the definition of entropy, it follows that

$$S = \int \frac{dQ}{dT} \frac{dT}{T} = C_P \ln \left( \frac{T_f}{T_i} \right). \quad (3.46)$$

### Adiabatic Process in Ideal Gas

Starting with the definition of entropy, an adiabatic process in ideal gas obeys

$$\begin{aligned} S &= \int \frac{dQ}{T} = \int \frac{dU + PdV}{T} \\ &= NK \int \left( \frac{f}{2} \frac{dT}{T} + \frac{dV}{V} \right) = 0, \end{aligned}$$

which evaluates to zero because the terms inside the integral are equal and opposite by Equation (3.32).

### Free Expansion of Ideal Gas

In discussing the free expansion of ideal gas, we found that no energy changes whatsoever, i.e.,  $\Delta U = \Delta Q = W = 0$ . However, we also found that ideal gas expansion is irreversible, so the entropy shouldn't be zero.

To calculate the entropy of free expansion of ideal gas, imagine the effort required to isothermally compress the gas to its original volume. This is precisely the same condition that gave us Equation (3.44), thus the entropy is

$$S = NK \ln \left( \frac{V_f}{V_i} \right) .$$

A change in entropy implies a change in the 'quality' of the energy in a system. This means ideal gas freely-expanding through a hole, as opposed to escaping into a vacuum, could instead be used to do something that keeps energy 'organized', such as to wind up a spring connected to a turbine.

### Entropy of Light

A 'gas' of photons, also referred to as blackbody radiation, is subject to entropy. Recall that Stefan's law (3.11) states that the rate of electromagnetic energy transfer is given by

$$\frac{dQ}{dt} = A\sigma (T_{\text{obj}}^4 - T_{\text{env}}^4) ,$$

where  $e = 1$  and for simplicity we'll take  $T_{\text{env}}$  to be constant. The total energy in a volume  $V$  of photon gas is

$$Q = \frac{\sigma}{c} (T_{\text{obj}}^4 - T_{\text{env}}^4) \int d^3x = \frac{V\sigma}{c} (T_{\text{obj}}^4 - T_{\text{env}}^4) ,$$

and it follows that  $dQ = (V\sigma/c)4T_{\text{obj}}^3 dT$ . Thus the entropy  $S$  as a function of  $T_{\text{obj}}$  is

$$S = \int \frac{dQ}{T} = \frac{4V\sigma}{c} \int T^2 dT = \frac{4V\sigma}{3c} (T_{\text{obj}}^3 - T_0^3) .$$

If we approximate  $T_{\text{env}} = 0$  and  $T_0 = 0$ , the entropy becomes

$$S = \frac{4}{3} \frac{Q}{T} .$$

## 4.2 Second Law of Thermodynamics

The *second law of thermodynamics* is a restriction on the entropy of closed systems. The following statements more-or-less equally capture the second law:

### Entropy statement

*The entropy of a closed system can never decrease. The entropy of an open system can be forced to decrease, but the net entropy of the system + surroundings necessarily increases.*

### Engine statement

*It is impossible for any system to undergo a cyclic process in which it absorbs heat at a single temperature and converts the heat completely into mechanical work.*

### Refrigerator statement

*It is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter body.*

## 4.3 Systems in Contact

Systems placed in contact will exchange energy, temperature, particles, and so on - depending on the intimacy of contact. Such conjoined systems always tend toward some kind of equilibrium state, and we take advantage of this to re-understand the notion temperature, pressure, etc.

### Thermal Equilibrium

Consider two thermodynamic systems  $A$  and  $B$  that are in separate, rigid, sealed containers. With  $T_A > T_B$  initially, the systems are then placed in contact to allow internal energy exchange by conduction or radiation, with the total  $U = U_A + U_B$  remaining constant.

A heat packet  $dQ = -dU_A = dU_B$  exchanged between systems changes the entropy of both:

$$dS_A = -\frac{|dQ|}{T_A}$$

$$dS_B = \frac{|dQ|}{T_B}$$

To accommodate the temperature terms, the entropy loss of the hotter system  $A$  is *smaller* in magnitude than the entropy gain of the cooler system  $B$ . The sum  $dS_A + dS_B$  is necessarily positive, thus the energy exchange is irreversible. *Thermal equilibrium* is achieved when the entropy stops increasing, corresponding to  $T_A = T_B = T$ , or

$$\frac{1}{T} = \frac{dS_A}{dU_A} = \frac{dS_B}{dU_B} = \frac{1}{T} .$$

### Definition of Temperature

Given the the role of entropy in thermal equilibrium, we seize this opportunity to actually *define* the notion of temperature as an entropy maximum with respect to internal energy (for fixed  $V$  and  $N$ ):

$$T = \left( \frac{\partial S}{\partial U} \right)^{-1}_{V,N} \quad (3.47)$$

### Mechanical Equilibrium

Supposing the partition between systems  $A$  and  $B$  were made flexible but not porous, the systems tend toward *mechanical equilibrium*, where maximum entropy corresponds to equal pressures. Supposing  $T_A = T_B$  with  $V_A > V_B$  initially, the heat packet exchanged between systems is purely mechanical as  $dQ = -P_A dV_A = P_B dV_B$ .

Using the same arguments as above, we may replace instances of  $dQ$  with  $PdV$  terms to get:

$$\frac{P}{T} = \frac{dS_A}{dV_A} = \frac{dS_B}{dV_B} = \frac{P}{T}$$

Alas, we're in position to relate pressure to entropy as we did the temperature. The equation

$$P = T \left( \frac{\partial S}{\partial V} \right)_{U,N} \quad (3.48)$$

describes systems with fixed internal energy and fixed number of particles. Note that the above is merely a tool for calculation, not a refined definition of pressure.

### Diffusive Equilibrium

We now let systems  $A$  and  $B$  exchange both energy and particles through a non-flexing porous membrane. Placed in contact, the systems achieve *diffusive equilibrium* in addition to thermal equilibrium.

The heat  $dQ$  exchanged between systems is proportional to the number of particles  $dN$  that move across the membrane. The proportionality factor between energy and particles is called the *chemical potential*, denoted  $\mu$ , as

$$dQ = \mu dN .$$

implying

$$\frac{-\mu}{T} = \frac{dS_A}{dN_A} = \frac{dS_B}{dN_B} = \frac{-\mu}{T} .$$

We thus define the *chemical potential* in terms of the entropy:

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,V} \quad (3.49)$$

The minus sign in Equation (3.49) reminds us that particles flow from regions of higher  $\mu$  to lower. When there are multiple particle species present in a system,  $\mu$  adopts a subscript  $j$  for each species, and the quantity  $\mu dN$  becomes  $\sum \mu_j dN_j$ .

## 5 Thermodynamic Variables

### 5.1 Extensive and Intensive

Most thermodynamic variables belong to one of two classifications. A quantity may be *extensive*, where the scale of the variable goes with the size of the system, or it may be *intensive*, where the scale of the variable doesn't care about the scale of the system. To illustrate, consider a thermodynamic system with the laundry list of state variables. If the system is duplicated and attached to itself, we ask which variables scale appropriately, versus which variables stay the same? You should conclude:

**Extensive:**  $M, V, N, U, S$

**Intensive:**  $P, T, \mu, \rho$

Properties of intensive and extensive variables:

- An extensive quantity multiplied by an intensive quantity yields an extensive quantity.
- The sum of two extensive quantities is also extensive.
- A ratio of extensive quantities yields an intensive quantity.
- The product of two extensive quantities is rare in calculations - check twice if you encounter this.
- The sum of an extensive quantity and an intensive quantity should never arise.

### 5.2 First Thermodynamic Identity

Recall the first law of thermodynamics as stated in Equation (3.28), namely

$$dU = dQ - PdV .$$

Our study of thermal and diffusive equilibrium has shown  $dQ$  coming in two flavors as  $dQ = TdS$  and  $dQ = \mu dN$ , respectively. It follows that the first law has a special form

$$dU = TdS - PdV + \mu dN , \quad (3.50)$$

which we'll call the *first thermodynamic identity*.

### Entropy of the Universe

The whole universe consists of any given system plus its total environment such that  $S_{\text{uni}} = S_{\text{sys}} + S_{\text{env}}$ . It follows that Equation (3.50) lets us write:

$$dS_{\text{uni}} = dS_{\text{sys}} + \left( \frac{1}{T} (dU + PdV - \mu dN) \right)_{\text{env}} \quad (3.51)$$

### 5.3 Free Energies

The meaning of the term *thermal energy* or *thermodynamic potential* can vary depending on the conditions surrounding a system. The distinction is characterized by the *free energy* of the system.

#### Enthalpy

In an environment with fixed pressure  $P$ , the total energy required to create a system with internal energy  $U$  and volume  $V$  is called the *enthalpy*, defined as

$$H = U + PV. \quad (3.52)$$

Enthalpy is the internal energy of a system plus the work required to shove the environment out of the way in order to make room the system. Conversely,  $H$  is the total energy recovered if you could annihilate the system.

#### Problem 50

Show that the enthalpy of an ideal gas is  $H = 5NKT/2$ .

The differential enthalpy is  $dH = dU + PdV + VdP$ , where substituting Equation (3.50) gives a new identity

$$dH = TdS + VdP + \mu dN. \quad (3.53)$$

The enthalpy is generally not extremized as the system tends toward equilibrium. In the special case that  $P$  and  $S$  are constant, the enthalpy is minimized at equilibrium.

#### Helmholtz Free Energy

In an environment with fixed temperature  $T$ , one who creates a system with constant  $V$  and constant  $N$  shall borrow energy from the environment by an amount equal to  $TS$ , where  $S$  is the entropy of the system. The net work required is therefore

$$A = U - TS, \quad (3.54)$$

called the *Helmholtz Free Energy*. This is the energy recovered if the system is destroyed in the same conditions.

The differential Helmholtz free energy is  $dA = dU - TdS - SdT$ , where substituting Equation (3.50) gives another identity

$$dA = -SdT - PdV + \mu dN. \quad (3.55)$$

By assuming the system has fixed  $T$ ,  $V$ ,  $N$ , we assume the same about the environment. In accordance with Equation (3.51), we have that a such a system plus its environment will follow

$$dS_{\text{uni}} = dS_{\text{sys}} + \left( \frac{1}{T} (dU + PdV - \mu dN) \right)_{\text{env}}.$$

The energy exchanged between the two are equal and opposite, i.e.  $dU_{\text{sys}} = -dU_{\text{env}}$ . All in terms of system variables, the above becomes

$$dS_{\text{uni}} = \frac{-1}{T} (dU - TdS).$$

On the right side of the above, the parenthesized expression is the differential Helmholtz free energy for constant  $T$ , i.e.

$$dS_{\text{uni}} = \frac{-1}{T} (dA)_{T,V,N}.$$

Thus, we find that such a system will do whatever it can to minimize the Helmholtz free energy.

#### Gibbs Free Energy

In an environment with fixed temperature  $T$  and pressure  $P$ , creating a system requires the *Gibbs free energy*

$$G = U + PV - TS, \quad (3.56)$$

which means you supply the internal energy  $U$  plus the work  $PV$  to shove the environment out of the way. The environment supplies  $TS$  for you, hence the minus sign. In the same conditions,  $G$  is the energy recovered if the system is annihilated.

Taking the differential Gibbs free energy and substituting (3.50) gives a corresponding identity:

$$dG = -SdT + VdP + \mu dN \quad (3.57)$$

At constant temperature and pressure, the  $dT$ - and  $dP$ -terms are zero, leaving us with  $dG = \mu dN$ , which integrates to

$$G = \mu N. \quad (3.58)$$

Notice this readily generalizes to a gas with multiple species of particles:

$$G = \sum_j \mu_j N_j$$

You might wish that a similar relation connects  $A$  to  $N$  by starting with  $\mu = (\partial A / \partial N)_{T,V}$ . However, adding particles while maintaining fixed  $T$  and

$V$  causes the density to slowly increase, which directly changes  $\mu$ .

Assume the system and the environment have fixed  $T$ ,  $P$ ,  $N$ . In accordance with Equation (3.51), we have that a such a system plus its environment will follow

$$dS_{\text{uni}} = dS_{\text{sys}} + \left( \frac{1}{T} (dU + PdV - \mu dN) \right)_{\text{env}} .$$

The energy and volume exchanged between the two are equal and opposite, i.e.  $dU_{\text{sys}} = -dU_{\text{env}}$ ,  $dV_{\text{sys}} = -dV_{\text{env}}$ . All in terms of system variables, the above becomes

$$dS_{\text{uni}} = \frac{-1}{T} (dU + PdV - TdS) .$$

On the right side of the above, the parenthesized expression is the differential Gibbs free energy for constant  $T$  and  $P$ , i.e.

$$dS_{\text{uni}} = \frac{-1}{T} (dG)_{T,P,N} .$$

Such a system will do whatever it can to minimize the Gibbs free energy. Note if  $T$  is allowed to vary, the system instead minimizes the enthalpy.

### Summary

The above is summarized as follows:

- Fixed  $U$ ,  $V$ :  
Maximize entropy ( $S$ ).
- Fixed  $P$ :  
Minimize enthalpy ( $H = U + PV$ ).
- Fixed  $T$ ,  $V$ :  
Minimize Helmholtz ( $A = U - TS$ ).
- Fixed  $T$ ,  $P$ :  
Minimize Gibbs ( $G = U + PV - TS$ ).

### Grand Free Energy

A grouping of terms useful for describing irreversible processes in open systems is the *grand free energy*, defined as

$$\Phi = U - TS - \mu N . \quad (3.59)$$

The quantity (3.59) is the energy recovered by reducing the system to zero size; putting all particles and energy back into the reservoir. Using Equation (3.58), it's straightforwardly shown that

$$\Phi = -PV . \quad (3.60)$$

Suppose a system of fixed  $V$  is allowed to exchange both  $U$  and  $N$  with its environment. Assume the chemical potential  $\mu$  of the system is already in equilibrium with the environment, as is the temperature  $T$ . The differential version of  $\Phi$  reads

$$d\Phi = dU - TdS - \mu dN ,$$

which is the right hand side of Equation (3.51). It immediately follows that

$$dS_{\text{uni}} = -\frac{1}{T} (d\Phi)_{T,V,\mu} ,$$

meaning a system with fixed  $V$  in thermal and diffusive equilibrium with the environment will minimize the grand free energy.

### Energy Checksum

A handy consistency check on the internal energy  $U$  can be derived in terms of  $TS$ ,  $PV$  and  $\mu N$ , avoiding terms like  $H$ ,  $A$ ,  $G$ , and  $\Phi$ . Start with the first thermodynamic identity

$$dU = TdS - PdV + \mu dN ,$$

and ask: which potential could be added to  $dU$  in order to make the right side a total derivative? Denoting such a term  $\Xi$ , we write

$$d(U + \Xi) = d(TS) - d(PV) + d(\mu N) ,$$

where clearly,

$$d\Xi = SdT - VdP + d\mu N .$$

Notice though that this is (minus) the differential version of  $\Phi + PV$ , which is identically zero, meaning that  $\Xi$  is exactly zero. Integrating the above gives

$$U = TS - PV + \mu N ,$$

the familiar formula for the Gibbs free energy.

### Gibbs-Duhem Equation

The arrangement of thermodynamic state variables that gives zero on either side of the equation gives a special result relating differential chemical potentials. Begin with the Grand free energy as given by (3.59), and add the  $PV$  term onto the left to get zero on the right:

$$\Phi + PV = U - TS - \sum_i \mu_i N_i + PV = 0$$

Note this discussion applies to a multi-species system, as indicated by the sum over particles with their

corresponding chemical potentials. Taking the differential version, we find

$$d(\Phi + PV) = -SdT + VdP - \sum_i d\mu_i N_i = 0,$$

where for conditions of constant temperature and constant pressure, we arrive at the *Gibbs-Duhem* equation:

$$\sum_i d\mu_i N_i = 0 \quad (3.61)$$

## 5.4 Legendre Transform

We have found that the energy state of a system is beholden to its (sometimes controlled) relationship with the environment. For example, at fixed temperature, volume, and number of particles, the best representation is the Helmholtz free energy  $A(T, V, N)$ . Here we address *why* to ever bother with different potentials - that is, why not simply write  $U = U(T, V, N)$  and deal with internal energy all the time?

Staying in the Helmholtz regime, to assign  $U$  as a function of  $T$  is patently incorrect, as temperature is already defined by Equation (3.47), namely

$$T = \left( \frac{\partial S}{\partial U} \right)^{-1}_{V,N}.$$

It is appropriate however to express the internal energy in terms of the entropy instead as  $U = U(S, V, N)$ . To proceed, consider a given point  $P$  on a  $U(S)$  curve, and determine the slope  $\partial U / \partial S = T$  at that point. Draw a straight line through point  $P$  having slope  $T$ , and extend the line until it hits the  $U$ -axis. The  $U$ -intercept is precisely the Helmholtz free energy  $A$ . That is, we have drawn the line

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

which is equivalent to the usual formula  $A = U - TS$ . Subtracting  $TS$  from  $U$  in this way is called the *Legendre transform*. A similar procedure extends to each of the thermodynamic potentials.

## 5.5 State Variables as Derivatives

Thermodynamic identities (3.50), (3.53), (3.55), and (3.57) can be arranged to express certain state variables. For completeness, these are:

$$\begin{aligned} dU &= TdS - PdV + \mu dN \\ dH &= TdS + VdP + \mu dN \\ dA &= -SdT - PdV + \mu dN \\ dG &= -SdT + VdP + \mu dN \end{aligned}$$

From these, one readily derives the following:

### Derivatives of Entropy

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V,N}$$

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

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

### Derivatives of Helmholtz

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

$$-P = \left( \frac{\partial A}{\partial V} \right)_{T,N}$$

$$\mu = \left( \frac{\partial A}{\partial N} \right)_{T,V}$$

### Derivatives of Gibbs

$$-S = \left( \frac{\partial G}{\partial T} \right)_{P,N}$$

$$V = \left( \frac{\partial G}{\partial P} \right)_{T,N}$$

$$\mu = \left( \frac{\partial G}{\partial N} \right)_{T,P}$$

### Heat Capacity

$$C_V = \left( \frac{\partial U}{\partial T} \right)_{V,N} = \frac{3}{2}NK$$

$$C_P = \left( \frac{\partial H}{\partial T} \right)_{P,N} = \frac{5}{2}NK$$

### Thermal Expansion

As a partial derivative, the coefficient of thermal expansion, namely  $\beta = 3\alpha$  from Equation (3.3) may be written as

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P.$$

A similar property of matter is the isothermal compressibility  $\kappa_T$ , defined as

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T.$$

**Problem 51**

Assume some equation of state (not necessarily the ideal gas equation) connects a system's pressure  $P$ , temperature  $T$ , and volume  $V$ . For the infinitesimal change  $P \rightarrow P + dP$ ,  $T \rightarrow T + dT$  with  $V$  fixed, (i) show that  $(\partial V/\partial P)_T dP + (\partial V/\partial T)_P dT = 0$ . (ii) Next show that

$$\frac{dP}{dT} = \left( \frac{\partial P}{\partial T} \right)_V = - \frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}.$$

**Problem 52**

Near room temperature, liquid water has a thermal expansion coefficient  $\beta = 2.5 \times 10^{-4} \text{ K}^{-1}$  and isothermal compressibility  $\kappa_T = 4.5 \times 10^{-10} \text{ Pa}^{-1}$ . Estimate the pressure that must be exerted on a drop of water in order to prevent it from expanding while increasing from  $20^\circ\text{C}$  to  $30^\circ\text{C}$ . Use this result to explain why it is easier to measure  $C_P$  rather than  $C_V$ . Answer: 55.8 atm

**Problem 53**

For a van der Waals fluid obeying Equation (3.27) at fixed  $T$  and  $N$ , use the thermodynamic identity (3.57) to show that the Gibbs free energy is:

$$G = -NKT \ln(V - Nb) + \frac{N^2 b K T}{V - Nb} - \frac{2aN^2}{V} + C(T) \quad (3.62)$$

From the rules of partial derivatives,  $dA$  also reads

$$dA = \left( \frac{\partial A}{\partial T} \right)_V dT + \left( \frac{\partial A}{\partial V} \right)_T dV,$$

where from calculus, we must have

$$\left( \frac{\partial}{\partial V} \left( \frac{\partial A}{\partial T} \right)_V \right)_T = \left( \frac{\partial}{\partial T} \left( \frac{\partial A}{\partial V} \right)_T \right)_V$$

Substituting state variables for the inner derivatives, but leaving the outer ones, we arrive at a *Maxwell relation*:

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad (3.63)$$

In the same spirit, we can do the same for  $dU$ ,  $dH$ , and  $dG$ , where the number of particles is fixed in all cases. Respectively, the results are:

$$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V \quad (3.64)$$

$$\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P \quad (3.65)$$

$$\left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P \quad (3.66)$$

## 5.6 Maxwell Relations

A trick from calculus allows a deeper relationship between derivatives and state variables. Consider a function  $f$  of two variables  $x$  and  $y$ . It's easy to see that the mixed second derivatives of  $f$  are identical:  $\partial_{xy}f = \partial_{yx}f$ . Applying this to thermodynamics, Take for example the differential Helmholtz free energy,  $dA$ , with a fixed number of particles. By Equation (3.55), we have

$$dA = -SdT - PdV.$$

## 6 Chemical Physics

### 6.1 Thermochemistry Tables

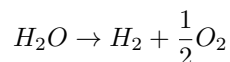
In response to change, a thermodynamic system's state variables will adjust in accordance with environmental conditions. At 'standard' room temperature (298 K) and at 'standard' atmospheric pressure (1 atm), also known as *STP* conditions, the enthalpy  $H$ , entropy  $S$ , and Gibbs free energy  $G$  of common substances behave as listed in the following *thermochemistry table*, also called an entropy table:

Symbol	Species	Enthalpy $\Delta H$ [kJ mol <sup>-1</sup> ]	Entropy $S$ [J mol <sup>-1</sup> K <sup>-1</sup> ]	Gibbs free energy $\Delta G$ [kJ mol <sup>-1</sup> ]
$H_2O$	Liquid Water	-285.83	69.95	-237.15
$H_2O$	Water Vapor	-241.83	188.84	-228.59
$H_2$	Hydrogen Gas	0	130.7	0
$O_2$	Oxygen Gas	0	205.07	0
$O$	Monatomic Oxygen	249.170	161.055	231.731
$N$	Nitrogen Gas	472.704	153.298	455.563
$NH_3$	Ammonia	-45.90	192.77	-16.37



## Electrolysis of Water

Consider a 1 mol sample of liquid water at standard temperature and pressure conditions. When electric current is applied through the sample, the reaction



takes place. Using the data above, we may calculate the energy required to drive the reaction.

Rummaging through the various energy quantities studied previously, observe that the enthalpy  $H = U + PV$  matches the scenario. From thermochemistry data, we find that the enthalpy decreases by  $\Delta H = -286$  kJ. (Note: of the 286 kJ that enters the system, an amount of work equal to  $1\text{ atm} \times \Delta V = 4\text{ kJ}$  is spent on shoving aside the atmosphere to make room for the new gases, with 282 kJ remaining.)

The entropy of the reaction is

$$\begin{aligned}\Delta S &= S_{H_2 + \frac{1}{2}O_2} - S_{H_2O} \\ &= \left(131 + \frac{205}{2} - 70\right) \text{ J K}^{-1} \\ &= 163 \text{ J K}^{-1},\end{aligned}$$

thus the environment contributes (positive) energy

$$T\Delta S = (298 \text{ K})(163 \text{ J K}^{-1}) = 49 \text{ kJ}.$$

Finally, the change in Gibbs free energy  $G = H - TS$  works out as  $\Delta G = \Delta H - T\Delta S = -286 \text{ kJ} + 49 \text{ kJ} = -237 \text{ kJ}$ , which ‘predicts’ the top-right value in the thermochemistry table. Evidently, the device driving electrolysis must only provide 237 kJ per mole of water.

## 6.2 Phase Change

At a boundary on a  $PT$  diagram, such as the gas-liquid boundary where the substance is stable in either form, the Gibbs free energy is the same on each side of the boundary:

$$G_{\text{gas}} = G_{\text{liquid}}$$

Using Equation (3.57) and noting that  $dG_{\text{gas}} = dG_{\text{liquid}}$ , we write for each side of the boundary (assuming  $N$  constant):

$$(-SdT + VdP)_{\text{gas}} = (-SdT + VdP)_{\text{liquid}}$$

Solving for  $dP/dT$ , one finds

$$\frac{dP}{dT} = \frac{S_{\text{gas}} - S_{\text{liquid}}}{V_{\text{gas}} - V_{\text{liquid}}} = \frac{\Delta S}{\Delta V}.$$

Next, recall that the latent heat of phase transformation at constant temperature is written  $L$ , which we interpret as equal to  $T\Delta S$ . From this we write

$$\frac{dP}{dT} = \frac{L}{T\Delta V},$$

also known as the *Clausius-Clapeyron relation*.

## Vapor Pressure

In the case that  $L$  is constant, and also that  $V_{\text{gas}} \gg V_{\text{liquid}}$  such that  $\Delta V \approx V_{\text{gas}} = V$ , we further assume that the evaporated gas is ideal gas. In this case, replace  $V$  to write

$$\frac{dP}{P} = \frac{L}{NK} \frac{dT}{T^2},$$

solved by

$$P = \psi e^{-L/NKT},$$

where  $\psi$  is a constant. Often, we set  $N$  to correspond to one mole of substance, and the final answer is written

$$P = \psi e^{-L/RT},$$

known as the *vapor pressure equation*.

## 6.3 Entropy of Mixing

Consider two systems such gases, equally-dense liquids, certain solids, or any other *ideal mixtures*  $A$  and  $B$  that are in thermal contact but in diffusive isolation by a partition. When the partition is removed, the change in entropy is strictly due to mixing, thus the analysis is highly analogous to ideal gas expansion. For each system respectively, start from Equation (3.44) to write

$$\begin{aligned}\Delta S_A &= N_A K \ln \left(1 + \frac{V_B}{V_A}\right) \\ \Delta S_B &= N_B K \ln \left(1 + \frac{V_A}{V_B}\right),\end{aligned}$$

and let  $y$  equal the volume and number ratio of species  $B$  to species  $A$ .

The sum  $\Delta S_A + \Delta S_B$  is the *entropy of mixing* formula:

$$\Delta S_{\text{mix}} = N_A K [(1-y) \ln(1-y) - y \ln y] \quad (3.67)$$

Letting  $\chi_\alpha$  equal the ratio the volume and number ratio of either species over the total, the above formula is equivalent to:

$$\Delta S_{\text{mix}} = -(N_A + N_B) K (\chi_A \ln \chi_A + \chi_B \ln \chi_B) \quad (3.68)$$

**Problem 54**

Show that the entropy of mixing for two equal portions  $N = N_A = N_B$  of ideal gas resolves to

$$\Delta S = 2NK \ln 2.$$

**Free Energy of a Mixture**

Consider (the same) two systems (gases, equally-dense liquids, certain solids)  $A$  and  $B$  that are in thermal contact but in diffusive isolation by a partition. Before the partition is removed, the Gibbs free energy is

$$G = \mu_A N_A + \mu_B N_B,$$

where letting  $N = N_A + N_B$  and  $x = N_B/N$ , we have

$$G = \mu_A N (1 - x) + \mu_B N x = (1 - x) G_A^0 + x G_B^0,$$

where  $G_A^0 = \mu_A N$  and  $G_B^0 = \mu_B N$  denote the unmixed energies. When the partition is removed, the total Gibbs free energy is simply

$$G_{\text{mix}} = (1 - x) G_A^0 + x G_B^0 + T \Delta S_{\text{mix}}. \quad (3.69)$$

**Dilute Solutions**

Consider a system that initially consists of  $N_A$  particles of species  $A$ . According to Equation (3.58), the Gibbs free energy reads

$$G = N_A \mu_0(T, P)$$

at fixed temperature and pressure. The volume of the system may be considered as the sum of  $N_A$  volume elements.

A single particle of species  $B$  added to the system will ‘freely expand’ (isothermally) into the existing volume in analogy to Equation (3.44), contributing  $-KT \ln(N_A)$  to the Gibbs free energy. The chemical binding energy is represented by some unknown function  $f(T, P)$ , so we write the energy change as

$$dG = f(T, P) - KT \ln(N_A).$$

Adding a second particle of species  $B$  is not a matter of taking  $dG \rightarrow 2dG$  due to the indistinguishability of particles. It follows that for two particles of species  $B$ , the total correction to the Gibbs free energy is

$$dG = 2f(T, P) - 2KT \ln N_A + KT \ln 2.$$

Generalizing to  $N_B$  particles while maintaining the dilute limit  $N_B \ll N_A$  particles is straightforward. The  $KT \ln 2$  term generalizes to

$KT \ln(N_B!)$ , which by Stirling’s approximation becomes  $KT(N_B \ln N_B - N_B)$ . Finally, we have the Gibbs free energy of a dilute solution,

$$G = N_A \mu_0(T, P) + N_B f(T, P) - N_B KT \ln N_A + N_B KT \ln N_B - N_B KT. \quad (3.70)$$

The chemical potentials of species  $A$  and  $B$  are readily calculated from the Gibbs free energy. These are:

$$\begin{aligned} \mu_A &= \left( \frac{\partial G}{\partial N_A} \right)_{T, P, N_B} \\ &= \mu_0(T, P) - \frac{N_B KT}{N_A} \end{aligned} \quad (3.71)$$

$$\begin{aligned} \mu_B &= \left( \frac{\partial G}{\partial N_B} \right)_{T, P, N_A} \\ &= f(T, P) + KT \ln \left( \frac{N_B}{N_A} \right) \end{aligned} \quad (3.72)$$

**6.4 Osmotic Pressure**

Consider a system of total volume  $V$  and number of particles solvent  $N_A$ . Next, divide the system with a semipermeable membrane and introduce some number of solute particles  $N_B$  on one side of the membrane. The membrane is tuned to allow the passage of solute particles, but not solvent particles. It follows that the pressure is weakly discontinuous across the membrane, and so too is the chemical potential on either side of the membrane, leading us to write

$$\mu_0(T, P_2) \approx \mu_0(T, P_1) + (P_2 - P_1) \frac{\partial \mu_0}{\partial P}.$$

Using Equation (3.71) for the chemical potential of the solvent particles, arrive at

$$(P_2 - P_1) \frac{\partial \mu_0}{\partial P} = \frac{N_B KT}{N_A}.$$

Of course, the derivative  $\partial \mu_0 / \partial P$  is simply  $V/N_A$  at constant  $T$  and  $N$ , and we arrive at

$$(P_2 - P_1) = \frac{N_B KT}{V}, \quad (3.73)$$

a result known as the *van’t Hoff* formula. The pressure difference  $P_2 - P_1$  is known as the *osmotic pressure*.

**6.5 Fugacity**

As a dilute solution tends to equilibrium, the pressure required for the system to become diffuse and behave like ideal gas is called the *fugacity*. Begin by considering the entropy of freely-expanding ideal gas

$$S = NK \ln \left( \frac{V_f}{V_i} \right),$$

which also obeys  $P_i V_i = P_f V_f$ . Next, insert  $S$  into the definition (3.49) of chemical potential to get

$$\mu = \mu_0 + KT \ln \left( \frac{P_f}{P_i} \right),$$

where the  $\mu_0$  term has been imposed into the equation to handle dilute solutions. The ideal gas has  $\mu_0 = 0$ .

The above result generalizes to multiple dilute solutions. Let the ‘initial’ pressure  $P_i$  equal the sum  $P$  of all partial pressures, so drop the subscript. The  $j$ -th partial substance thus obeys

$$\mu_j = \mu_0 + KT \ln \left( \frac{P_j}{P} \right), \quad (3.74)$$

which generalizes again to non-ideal gases by introducing a van der Waals constant  $b$  as

$$\mu_j = \mu_0 + KT \ln \left( \frac{P_j}{P} \right) + bP,$$

which is equivalent to adding a dimensionless term  $\phi$  into the ln-term of Equation (3.74). Note that we

have deployed a simplified van der Waals equation  $P(V - Nb) = NKT$ .

#### Problem 55

Show that:

$$bP = KT \ln \phi$$

The dimensionless quantity  $\phi$  is called the *fugacity coefficient*, and the bare term ‘fugacity’ typically refers to the modified pressure

$$f = \phi P. \quad (3.75)$$

Fugacity comes into play when describing non-ideal gases near the ideal gas limit. Paraphrasing the differential version of Equation (3.74) for one chemical species, we define a formula that *replaces* pressure with fugacity:

$$d\mu = KT d(\ln f) \quad (3.76)$$

Immediately following definition (3.76), we solve for  $f$  to write

$$f = \exp \left( \frac{\mu - \mu_0}{KT} \right).$$

## Chapter 4

# Variational Mechanics

## Chapter 5

# Classical Field Theory

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