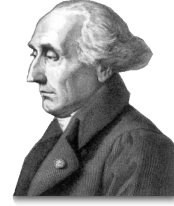


Coupled Oscillators

Wednesday, 26 October 2011

Physics 111



In which we count degrees of freedom and find the normal modes of a mess o' masses and springs, which is a lovely model of a solid.

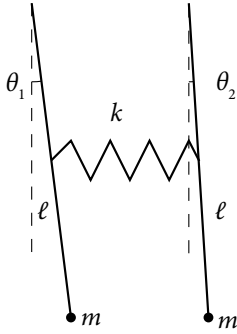


Figure 1: Two simple pendulums coupled by a weak spring.

Two pendulums coupled with a spring may oscillate at the same frequency in two ways: the “parallel play” mode, in which the two pendulums move back and forth maintaining a constant distance between them, and the love-hate relationship, in which they move in opposition. This latter mode oscillates at higher frequency.

Suppose that the pendulums have length ℓ , mass m , and are linked by a spring of spring constant k at their midpoints. Taking the zero of potential energy at the point of suspension of the pendulums, the Lagrangian of this system is approximately

$$L = \frac{1}{2} m \ell^2 (\dot{\theta}_1^2 + \dot{\theta}_2^2) + mg\ell(\cos \theta_1 + \cos \theta_2) - \frac{1}{2} k \left(\frac{\ell}{2} \right)^2 (\theta_1 - \theta_2)^2 \quad (1)$$

where I have neglected the vertical displacement of the ends of the springs and approximated their horizontal displacement as $\ell\theta/2$. In fact, in this approximation, the cosine terms may be simplified to their lowest nontrivial dependence on each angle, giving (up to a constant)

$$L = \frac{1}{2} m \ell^2 (\dot{\theta}_1^2 + \dot{\theta}_2^2) - \frac{mg\ell}{2} (\theta_1^2 + \theta_2^2) - \frac{1}{2} k \left(\frac{\ell}{2} \right)^2 (\theta_1 - \theta_2)^2 \quad (2)$$

The Lagrange equations for this system are therefore

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\theta}_1} \right) - \frac{\partial L}{\partial \theta_1} = m \ell^2 \ddot{\theta}_1 + mg\ell\theta_1 + \frac{k\ell^2}{4} (\theta_1 - \theta_2) = 0 \quad (3)$$

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\theta}_2} \right) - \frac{\partial L}{\partial \theta_2} = m \ell^2 \ddot{\theta}_2 + mg\ell\theta_2 + \frac{k\ell^2}{4} (\theta_2 - \theta_1) = 0 \quad (4)$$

Divide these equations by $m\ell^2$ to tidy them up a bit:

$$\ddot{\theta}_1 + \frac{g}{\ell} \theta_1 + \frac{k}{4m} (\theta_1 - \theta_2) = 0 \quad (5)$$

$$\ddot{\theta}_2 + \frac{g}{\ell} \theta_2 + \frac{k}{4m} (\theta_2 - \theta_1) = 0 \quad (6)$$

What happens to these equations if $\theta_1(t) = \theta_2(t)$? Then the coupling terms disappear and we are left with identical simple harmonic oscillator equations. So, we deduce that one solution is of the form

$$\theta_1 = \theta_2 = c_1 \cos(\omega_0 t + \phi_1) = d_1 \cos \omega_0 t + d_2 \sin \omega_0 t \quad (7)$$

where $\omega_0^2 = g/\ell$, and c_1 and ϕ_1 (or equivalently d_1 and d_2) are constants to be determined by initial conditions.

A second solution may be found by assuming that $\theta_1 = -\theta_2$. Then the first equation becomes

$$\ddot{\theta}_1 + \frac{g}{\ell}\theta_1 + \frac{k}{2m}\theta_1 = 0$$

which is also the simple harmonic oscillator equation, with solution

$$\theta_1 = -\theta_2 = c_2 \cos(\omega_1 t + \phi_2) \quad (8)$$

where $\omega_1 = \sqrt{\frac{g}{\ell} + \frac{k}{2m}}$, and c_2 and ϕ_2 are constants.

The two boxed equations are the two **normal modes** of the coupled pendulum system. In a normal mode, all the particles oscillate at the same frequency (but not necessarily the same amplitude or phase). The general solution is a superposition of the two normal modes, with amplitudes and phases chosen to match the given initial conditions.

Example 1

At $t = 0$ we thump the first mass. What is the subsequent motion?

We'll assume that the thump takes place over negligible time, and serves to launch m_1 at some initial angular velocity $\dot{\theta}_1(0) = \Omega$. If the first normal mode is described by $d_1 \cos \omega_0 t + d_2 \sin \omega_0 t$, while the second is described by $d_3 \cos \omega_1 t + d_4 \sin \omega_1 t$, then

$$\begin{aligned} \theta_1(0) &= d_1 + d_3 & \dot{\theta}_1(0) &= d_2 \omega_0 + d_4 \omega_1 = \Omega \\ \theta_2(0) &= d_1 - d_3 & \dot{\theta}_2(0) &= d_2 \omega_0 - d_4 \omega_1 = 0 \end{aligned}$$

The angular positions require that $d_1 = d_3 = 0$, while the angular velocities require that $d_2 \omega_0 = d_4 \omega_1 = \Omega/2$. Therefore,

$$\theta_1(t) = \frac{\Omega}{2\omega_0} \sin \omega_0 t + \frac{\Omega}{2\omega_1} \sin \omega_1 t \quad (9)$$

$$\theta_2(t) = \frac{\Omega}{2\omega_0} \sin \omega_0 t - \frac{\Omega}{2\omega_1} \sin \omega_1 t \quad (10)$$

For weak coupling, ω_1 is not much greater than ω_0 , so the two terms beat at a frequency given by the difference between ω_1 and ω_0 ; **the energy is gradually traded from one oscillator to the other and back.**

1. Generalization to N Coupled Particles

We now wish to generalize this example to a system of N masses coupled with various springs to form a molecule or solid with a stable equilibrium configuration. On perturbing one or more of the masses from equilibrium, what sort of motion arises?

If the system is three-dimensional, we will need $3N$ generalized coordinates q_j to describe the configuration of the system, and a corresponding number of generalized velocities $\dot{q}_j$. Of the $3N$ degrees of freedom, 3 correspond to the center of mass translation of the system, and 3 to its rotation (unless the system happens to be a linear molecule, in which case the molecule can rotate only about two axes). None of these coordinates has a restoring force; absent external influences, their momenta will be constants of the motion. This leaves $3N - 6$ ($3N - 5$) degrees of freedom associated with distortions away from equilibrium positions. We will show that each of these gives rise to a **normal mode** of vibration, in which all the masses oscillate at the same frequency. Furthermore, each normal mode is independent of all the others, so that the $3N - 6$ coupled oscillators factor into $3N - 6$ decoupled (independent) oscillators.

So, are the motions associated with center-of-mass translation and rigid-body rotation “normal modes”? I’m not sure that the literature is consistent on this point. In some sense, these motions are normal modes, since all the particles move with the same (zero) frequency and the same velocity (or angular velocity). The crucial point, however, is not whether they are or are not called normal modes. Rather, it is to keep careful track of the number of degrees of freedom to make sure that they are all accounted for somewhere, either in a normal mode with nonzero frequency or in one of these “special” modes describing translation or rotation.

We will work in the center of mass frame and disregard rotation. Then in the equilibrium configuration,

$$q_j = q_{j0}, \quad \dot{q}_j = 0, \quad \ddot{q}_j = 0, \quad j = 1, 2, \dots, n$$

where $n = 3N - 6$ (or $3N - 5$ if linear). Lagrange’s equation for the j th coordinate is,

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} = 0$$

The first term must contain either $\dot{q}_j$ or $\ddot{q}_j$, both of which vanish. Therefore, $\frac{\partial L}{\partial q_j} = \frac{\partial U}{\partial q_j} = 0$. With no loss of generality, we may shift the origin of each generalized coordinate to q_{j0} . Then expanding the potential about the equilibrium position in a Taylor series through second order, we have

$$\begin{aligned} U(q_1, q_2, \dots, q_n) &= U_0 + \sum_j \left. \frac{\partial U}{\partial q_j} \right|_0 q_j + \frac{1}{2} \sum_{j,k} \left. \frac{\partial^2 U}{\partial q_j \partial q_k} \right|_0 q_j q_k + \dots \\ &\approx U_0 + \frac{1}{2} A_{jk} q_j q_k \end{aligned} \quad (11)$$

where we use the summation convention in the final expression (and henceforth). The linear term vanishes in equilibrium because we are at a potential minimum. Apart from the constant term in front, Eq. (11) says that for small displacements from equilibrium the potential

energy increases quadratically with the displacement, no matter in which combination of generalized coordinates we make the displacement.

Furthermore, if the equations of transformation are not explicit functions of the time, then the kinetic energy is a homogeneous quadratic function of the generalized velocities,¹

$$T = \frac{1}{2} m_{jk} \dot{q}_j \dot{q}_k \quad (14)$$

Therefore, if all the displacements from equilibrium are small enough that the quadratic approximation to the potential is valid, the Lagrangian of the system is expressible in terms of two symmetric $n \times n$ matrices, the mass matrix m_{jk} and the spring matrix A_{jk} , as

$$L = T - U = \frac{1}{2} m_{jk} \dot{q}_j \dot{q}_k - \frac{1}{2} A_{jk} q_j q_k \quad (15)$$

Lagrange's equations are thus

$$\boxed{A_{jk} q_j + m_{jk} \ddot{q}_j = 0} \quad (16)$$

This is a set of n coupled second-order differential equations, since $k = 1, 2, \dots, n$.

To solve Eq. (16), we use our experience with oscillatory systems and guess that we can find solutions that oscillate sinusoidally in time. We will hope that we can find solutions in which every particle oscillates at the same frequency. So, we guess $q_j = a_j e^{-i\omega t}$, which allows us to convert the coupled second-order differential equations into coupled *linear* equations in the square of the angular frequency ω :

$$(A_{jk} - \omega^2 m_{jk}) a_j = 0 \quad \text{or} \quad (\mathbb{A} - \omega^2 \mathbb{M}) \mathbf{a} = 0 \quad (17)$$

where the second form is written as an explicit matrix equation. For a nontrivial solution, the determinant $|\mathbb{A} - \omega^2 \mathbb{M}|$ must vanish, which is an n th order equation for ω^2 called the **characteristic equation** or the **secular equation**. It therefore has n roots (some of which may be degenerate). Because $\mathbb{A}$ and $\mathbb{M}$ are real, symmetric matrices, and because $T \geq 0$, it is possible to show that

1. all the eigenvalues ω^2 are real and positive;

¹If the system comprises N particles whose Cartesian coordinates are $x_{\alpha,i}$, with $\alpha = 1, 2, \dots, N$ and $i = 1, 2, 3$ indexing the component of the Cartesian position vector of the α th particle, then

$$T = \sum_{\alpha=1}^N \sum_{i=1}^3 \frac{1}{2} m_{\alpha} \dot{x}_{\alpha,i}^2 \quad (12)$$

Expressing the positions in terms of generalized coordinates, and assuming that the equations of transformation are not explicit functions of time, we have

$$T = \sum_{\alpha=1}^N \frac{1}{2} m_{\alpha} \left(\frac{\partial x_{\alpha,i}}{\partial q_j} \dot{q}_j \right) \left(\frac{\partial x_{\alpha,i}}{\partial q_k} \dot{q}_k \right) = \frac{1}{2} \sum_{j,k} m_{jk} \dot{q}_j \dot{q}_k \quad (13)$$

where $m_{jk} \equiv \sum_{\alpha} m_{\alpha} \frac{\partial x_{\alpha,i}}{\partial q_j} \frac{\partial x_{\alpha,i}}{\partial q_k}$, and a sum over Cartesian index i is implied.

2. the eigenvectors $\mathbf{a}_r$ are orthogonal, and can be normalized to yield an orthonormal basis, $\mathbf{a}_r = a_{rj}\mathbf{e}_j$; and
3. the configuration of the system may be expressed in terms of the normalized eigenvectors using **normal coordinates**, η_r , which satisfy $\ddot{\eta}_r + \omega_r^2 \eta_r = 0$, where ω_r is the corresponding eigenfrequency, $q_j(t) = \text{Re}(\sum_r a_{jr} \eta_r e^{-i\omega_r t})$.

Thus, the complicated system of $3N$ degrees of freedom reduces to $3N - 6$ normal modes in each of which all masses oscillate at the same frequency, 3 degrees of freedom for the center-of-mass translation, and 3 degrees of freedom for rigid-body rotation.

2. Linear Algebra

Perhaps you are so familiar with linear algebra that the above consequences are obvious. If so, you had a much better course than I did (which, frankly, isn't saying much)! You can skip to the next section.

In the following I will omit the summation signs and use the Einstein summation convention, so that Eq. (11) is

$$U - U_0 = \frac{1}{2} A_{jk} q_j q_k \geq 0 \quad (18)$$

and Eq. (17) is

$$(A_{jk} - \omega^2 m_{jk}) a_k = 0$$

We would like to show that ω^2 is real and positive, as we fully expect on physical grounds. Multiply by the complex conjugate of a_j and sum over j :

$$A_{jk} a_j^* a_k = \omega^2 m_{jk} a_j^* a_k \quad \implies \quad \omega^2 = \frac{A_{jk} a_j^* a_k}{m_{jk} a_j^* a_k}$$

Both the numerator and denominator have the same form, which we would like to show is both real and positive. To show that the numerator is real, take its complex conjugate:

$$\begin{aligned} (A_{jk} a_j^* a_k)^* &= A_{jk}^* a_j a_k^* && \text{taking conjugate} \\ &= A_{kj} a_j a_k^* && A_{jk} \text{ is real and symmetric} \\ &= A_{kj} a_k^* a_j && \text{exchange terms} \\ (A_{jk} a_j^* a_k)^* &= A_{jk} a_j^* a_k && \text{relabel indices} \end{aligned}$$

Thus, the numerator is equal to its complex conjugate, and similarly for the denominator. Hence, ω^2 is real.

To show that each of the quadratic sums is positive, express the complex coefficient $a_j = \alpha_j + i\beta_j$, for α_j and β_j real. Then

$$\begin{aligned} A_{jk} a_j^* a_k &= A_{jk} (\alpha_j - i\beta_j)(\alpha_k + i\beta_k) \\ &= A_{jk} \alpha_j \alpha_k + A_{jk} \beta_j \beta_k + i(A_{jk} \alpha_j \beta_k - A_{jk} \alpha_k \beta_j) \end{aligned}$$

The term in parentheses vanishes because $A_{jk} = A_{kj}$, which allows us to exchange $j \leftrightarrow k$ and put the second term in the same form as the first. By Eq. (18), each of the remaining terms is positive definite for real coefficients α_j and β_j . Hence, ω^2 is real and positive definite, so the eigenfrequencies are positive definite, also.

To show that the eigenvectors are orthogonal, assume that we have two distinct eigenfrequencies, ω_r and ω_s :

$$\begin{aligned}(A_{jk} - \omega_s^2 m_{jk})a_{ks} &= 0 \\ (A_{kj} - \omega_r^2 m_{kj})a_{jr} &= 0\end{aligned}$$

Because both A_{jk} and m_{jk} are symmetric, I can rewrite the second equation as

$$(A_{jk} - \omega_r^2 m_{jk})a_{jr} = 0$$

Now multiply the first equation by a_{jr} and sum, multiply the second by a_{ks} and sum, and subtract the results to get

$$(\omega_r^2 - \omega_s^2)m_{jk}a_{jr}a_{ks} = 0 \quad (19)$$

When $\omega_s \neq \omega_r$, this implies that

$$m_{jk}a_{jr}a_{ks} = 0 \quad (\omega_r \neq \omega_s) \quad (20)$$

which is the orthogonality condition. If $\omega_r = \omega_s$, then we can't tell about $m_{jk}a_{jr}a_{ks}$ from Eq. (19). If $r = s$, however, it is a quadratic form, which we have shown must be positive definite. We are free to normalize the eigenvector so that it has unit length. When there are multiple modes with the same frequency, it is always possible to diagonalize this subspace to produce orthogonal eigenvectors. Hence, the normalized eigenvectors satisfy

$$\boxed{m_{jk}a_{jr}a_{ks} = \delta_{rs}} \quad (21)$$

where δ_{rs} is the Kronecker delta.

Example 2

Find the vibration frequencies and normal modes of CO_2 .

Let the mass of the central carbon atom be M , the mass of the oxygen atoms be m , and the spring constant of the C–O bond be k . Align the molecule with the x axis and assume it is not rotating. Working in the center of mass frame, we have

$$\sum_{i=1}^3 m_i \mathbf{r}_i = 0 = m(\mathbf{r}_1 + \mathbf{r}_3) + M\mathbf{r}_2 \quad (22)$$

2.1 Longitudinal Vibrations

Consider first a motion purely along the axis of the molecule. We should anticipate a mode in which the carbon stays put and the two oxygens oscillate out of phase with one another. This mode should have the frequency $\sqrt{k/m}$, since it is as though the oxygen atom is bound by a spring to a fixed wall. The other mode should involve the oxygen atoms heading left when the carbon heads right, and should be at higher frequency, because both springs work to restore the carbon to its equilibrium position.

$$m(x_1 + x_3) = -Mx_2 \quad \implies \quad x_2 = -\mu(x_1 + x_3)$$

where $\mu \equiv m/M$. so that we may write the kinetic energy

$$T = \frac{m}{2}(\dot{x}_1^2 + \dot{x}_3^2) + \frac{M}{2}\dot{x}_2^2 = \frac{m}{2}[(1 + \mu)(\dot{x}_1^2 + \dot{x}_3^2) + 2\mu\dot{x}_1\dot{x}_3]$$

Hence,

$$m_{jk} = m \begin{pmatrix} 1 + \mu & \mu \\ \mu & 1 + \mu \end{pmatrix}$$

Notice that we have to divide the cross term equally between m_{12} and m_{21} , since m_{ij} is a symmetric matrix. Similarly, the potential energy is

$$U - U_0 = \frac{k}{2}[(x_2 - x_1)^2 + (x_3 - x_2)^2] = \frac{k}{2}[(2\mu^2 + 2\mu + 1)(x_1^2 + x_3^2) + 4\mu(\mu + 1)x_1x_3]$$

so

$$A_{jk} = k \begin{pmatrix} 2\mu^2 + 2\mu + 1 & 2\mu(\mu + 1) \\ 2\mu(\mu + 1) & 2\mu^2 + 2\mu + 1 \end{pmatrix}$$

The characteristic equation is $(A_{jk} - \omega^2 m_{jk})a_k = 0$, so that for a nontrivial solution we must have

$$\begin{vmatrix} k(2\mu^2 + 2\mu + 1) - m(1 + \mu)\omega^2 & 2k\mu(\mu + 1) - m\mu\omega^2 \\ 2k\mu(\mu + 1) - m\mu\omega^2 & k(2\mu^2 + 2\mu + 1) - m(1 + \mu)\omega^2 \end{vmatrix} = 0 \quad (23)$$

which means that

$$\begin{aligned} k(2\mu^2 + 2\mu + 1) - m(1 + \mu)\omega^2 &= \pm [2k\mu(\mu + 1) - m\mu\omega^2] \\ k[1 + \mu(\mu + 1)(2 \mp 2)] &= m\omega^2(1 + \mu \mp \mu) \\ \omega^2 &= \frac{k}{m} \frac{1 + (2 \mp 2)\mu(\mu + 1)}{1 + \mu \mp \mu} \end{aligned}$$

Thus, the two frequencies are

$$\boxed{\omega_- = \sqrt{\frac{k}{m}} \quad \text{and} \quad \omega_+ = \sqrt{\frac{k}{m}} \sqrt{1 + 2\mu}}$$

Before substituting the eigenvalues back into the determinant to find the eigenvectors (normal mode displacement amplitudes), let's pull out a common factor of k/m to get

$$\frac{k}{m} \begin{vmatrix} 2\mu^2 + 2\mu + 1 - m\omega^2/k & 2\mu(\mu + 1) - \mu m\omega^2/k \\ 2\mu(\mu + 1) - \mu m\omega^2/k & 2\mu^2 + 2\mu + 1 - m\omega^2/k \end{vmatrix} \quad (24)$$

Substituting ω_- into the secular determinant to solve for the eigenvector, we get

$$2k\mu(\mu + 1) \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} a_{-1} \\ a_{-3} \end{pmatrix} = 0 \quad \implies \quad a_- = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Sure enough, in this mode the displacements of the two oxygen atoms are equal and opposite.

Substituting ω_+ into the secular determinant to solve for the eigenvector, we get

$$\frac{2k\mu}{m} \begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} a_{-1} \\ a_{-3} \end{pmatrix} = 0 \quad \implies \quad a_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

We may readily confirm that these eigenvectors are orthogonal:

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \end{pmatrix} m \begin{pmatrix} 1 + \mu & \mu \\ \mu & 1 + \mu \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = 0$$

2.2 Transverse Vibrations

For motion perpendicular to the molecular axis, the zero-rotation condition requires that $y_1 = y_3$ and since $m(y_1 + y_3) + My_2 = 0$, that $y_2 = -\frac{2m}{M}y_1 = -2\mu y_1$. The kinetic energy is

$$T = \frac{m}{2} [2\dot{y}_1^2 + \mu^{-1}\dot{y}_2^2] = \frac{m}{2} [2\dot{y}_1^2 + 4\mu\dot{y}_1^2] = m\dot{y}_1^2(1 + 2\mu)$$

Using the Pythagorean theorem, we can compute the stretch of the springs as $\xi = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2} - (x_2 - x_1)$. Let $\ell = x_2 - x_1$ be the bond length. Then

$$\begin{aligned} U &= 2\frac{k}{2} \left[\ell^2 + y_1^2(1 + 2\mu)^2 + \ell^2 - 2\ell\sqrt{\ell^2 + y_1^2(1 + 2\mu)^2} \right] \\ &= 2k\ell^2 \left[1 + \frac{y_1^2(1 + 2\mu)^2}{2\ell^2} - \sqrt{1 + \frac{y_1^2(1 + 2\mu)^2}{\ell^2}} \right] \\ &\approx 0 + \mathcal{O}(y_1^4) \end{aligned}$$

where I have used the binomial approximation to simplify the radical. That is, if we just consider the stretch of the spring, we get nothing until order y_1^4 . That's not too promising.

If we consider, instead, that the molecule likes to be straight and that it experiences a restoring torque proportional to the bending angle, then

$$U \propto \left(\frac{y_1 - y_2}{\ell} \right)^2 = \left[\frac{y_1(2\mu + 1)}{\ell} \right]^2$$

where ℓ is the bond length. Let us suppose that the constant of proportionality is

$$U = 2 \times \frac{1}{2} k(\gamma^2 \ell^2) \left[\frac{y_1(2\mu + 1)}{\ell} \right]^2 = k\gamma^2 [y_1(2\mu + 1)]^2 \quad (25)$$

where γ is a dimensionless constant that compares the bending stiffness to the stretching stiffness of the bond. The energy of the molecule in this mode is thus

$$E = T + U = m\dot{y}_1^2(1 + 2\mu) + k\gamma^2(2\mu + 1)^2 y_1^2$$

Taking the ratio of the coefficient of the y_1^2 term to the $\dot{y}_1^2$ term gives the square of the transverse vibration frequency,

$$\omega_T^2 = \frac{k\gamma^2(1 + 2\mu)^2}{m(1 + 2\mu)} \quad \Longrightarrow \quad \boxed{\omega_T = \gamma \sqrt{\frac{k}{m}} \sqrt{1 + 2\mu}}$$

Now it is time to touch base with reality. The observed vibration frequencies of carbon dioxide are 667 : 1288 : 2349 (cm⁻¹). Note that I have quoted the vibration frequencies in the unit chemists and molecular spectroscopists seem to prefer: wave numbers. These correspond to wavelengths 14.99, 7.76, and 4.26 μm , in the spectral region of the thermal (re)radiation from the Earth.

The absorption bands of atmospheric gases are shown in Fig. 2. Carbon dioxide absorbs strongly near 15 μm and also near 4.5 μm . Only two of the three vibrational modes are “optically active,” meaning that they have a time-changing electric dipole moment and therefore couple strongly to electromagnetic radiation. When a light wave with the same frequency passes over the molecule, the electric field in the wave pushes positive and negative charges in opposite directions. Since oxygen is more electronegative than carbon, the carbon atom is slightly positively charged and the oxygen atoms slightly negatively charged. To a good approximation, the charge centers follow their respective nuclei as the molecule vibrates, and so the modes with nonzero dipole moment couple strongly to the electromagnetic field in the neighborhood of their resonant frequency. These are the transverse mode and the higher-frequency longitudinal mode. Evidently, therefore, we must associate the mode at 7.76 μm with the optically inert longitudinal mode of frequency $\sqrt{k/m}$, which implies that the high-frequency mode should be at

$$\lambda = 7.76 \mu\text{m} \left(1 + 2\frac{16}{12} \right)^{-1/2} = 4.05 \mu\text{m}$$

which is close. The mode at lowest frequency, $\lambda = 14.99 \mu\text{m}$, is associated with the transverse (bending) vibration, from which we infer $\gamma \approx 667/2349 = 0.284$. That is, the spring is significantly softer in bending than in stretching, which seems perfectly reasonable.

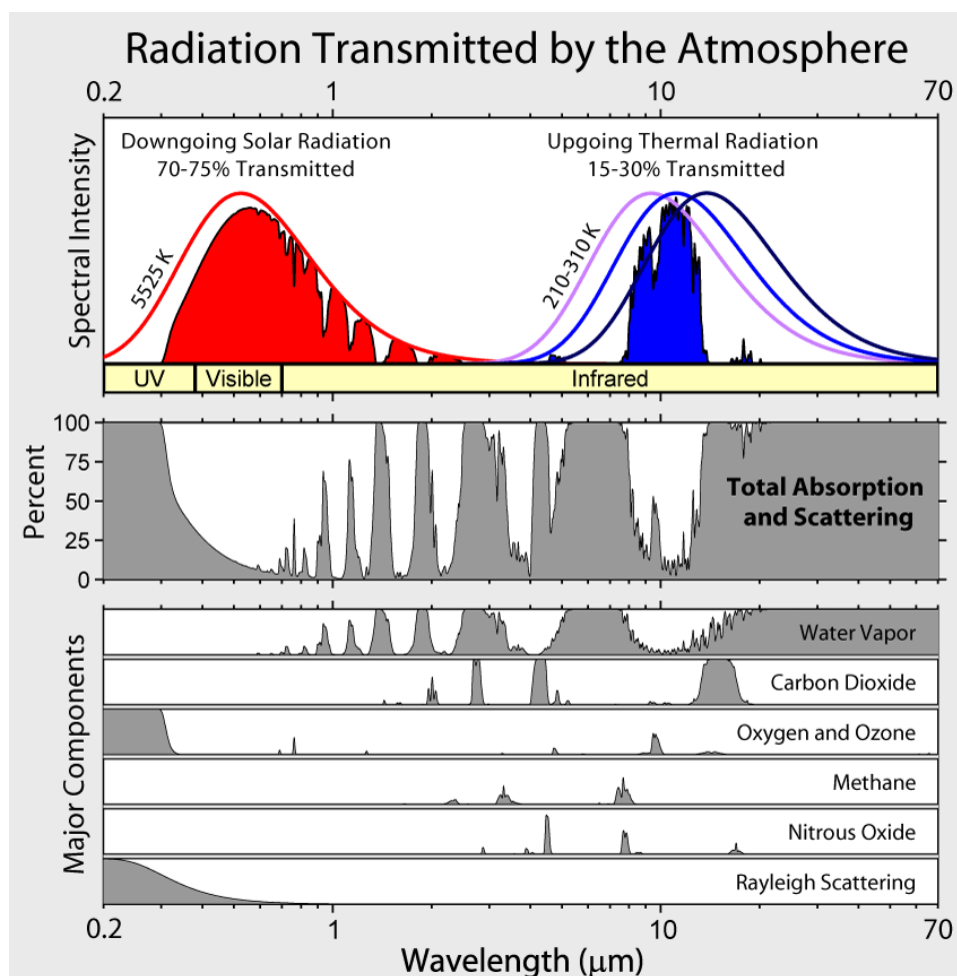


Figure 2: Atmospheric transmission