Lennard-Jones interatomic potential $V_{LJ}(r)$

$$V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

The minimum is at $r_0 = 2^{1/6}\sigma$

$$V(r) = \epsilon \left[ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right]$$

If a particle in this potential has energy $E>0$, it is unbound. If the energy obeys $-\epsilon<E<0$, then it oscillates between $x_1$ and $x_2$. 
Classical harmonic oscillator has a natural scale of time ($\omega^{-1}$) but no natural scale of distance. $A$ is arbitrary. Excitation energy $E - V_0 = kA^2/2$ is also.

Energy is conserved.

$$E = \frac{M}{2} \left( \frac{dr}{dt} \right)^2 + V(r)$$

Solve for $dt$ and integrate.

$$t - t_0 = \int_{t_0}^{t} dt = \int_{r(t_0)}^{r(t)} \frac{dr}{\sqrt{2(E - V(r))/M}}$$

If $V(r) = V_0 + kr^2/2$ then

$$r - r_0 = A \cos(\omega t + \phi)$$

where $\omega = \sqrt{k/M}$.

Harmonic spring const $k=72\varepsilon/r_0^2$

Excitation energy
\[ \mathcal{H} = p^2/2M + kx^2/2 \]

Add quantum mechanics. Operators \( p, x \):

\[ [p, x] \equiv px - xp = \hbar/i \quad \text{implies} \quad p = (\hbar/i) \partial/\partial x \]

Time-dependent Schrödinger Eqn.

\[ i\hbar \frac{\partial \psi}{\partial t} = \mathcal{H} \psi \]

Stationary solutions.

If \( \mathcal{H} \psi_n = E_n \psi_n \) then \( \psi_n(t) = \psi_ne^{-iE_n t/\hbar} \)

The new constant \( \hbar \), together with \( k \) and \( M \),

define scales of length, time, and energy.

\[ x \sim \sqrt{2\hbar/M\omega} \equiv a_0 \]

\[ p \sim \sqrt{2\hbar M\omega} = M\omega a_0 \]

\[ E \sim kx^2/2 \sim p^2/2M \sim \hbar\omega \]

Quantum Harmonic Oscillator

Factorize the Hamiltonian.

\[
\begin{align*}
\mathcal{H} &= \left( \frac{p}{M\omega a_0} \right)^2 + \left( \frac{x}{a_0} \right)^2 = \frac{1}{2}(aa^\dagger + a^\dagger a) \\
\hat{a} &= \frac{x}{a_0} + i\frac{p}{M\omega a_0} \\
a^\dagger &= \frac{x}{a_0} - i\frac{p}{M\omega a_0} \\
[a, a^\dagger] &= \frac{2i}{M\omega a_0^2}[p, x] = 1
\end{align*}
\]

\[
\frac{1}{2}(aa^\dagger + a^\dagger a) = a^\dagger a + \frac{1}{2} \\
\mathcal{H} = \hbar\omega(a^\dagger a + \frac{1}{2})
\]

Ground State

\[ \psi_0 \equiv |0\rangle \sim e^{-\frac{1}{2}(x/a_0)^2} \]

Excited States

\[ a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \quad a|n\rangle = \sqrt{n}|n-1\rangle \]

\[ \mathcal{H}|n\rangle = \hbar\omega(n + \frac{1}{2})|n\rangle \]

Level spacing \( E_{n+1} - E_n = \hbar\omega \)
Boltzmann weight $P_n = e^{-E_n/k_BT}/Z$

Partition function $Z = \sum_n e^{-E_n/k_BT}$

Thermodynamics $Z = e^{-F/k_BT} = 2/\sinh(\hbar\omega/2k_BT)$ (Harmonic oscillator)

Specific Heat $C = k_B \left[ \frac{(\hbar\omega/2k_BT)}{\sinh(\hbar\omega/2k_BT)} \right]^2 \rightarrow k_B$ (high $T$ classical limit)

mean excitation level $\bar{n} = \frac{1}{e^{\hbar\omega/k_BT} - 1}$ Planck – Bose – Einstein

Classical limit $\bar{n} + \frac{1}{2} \rightarrow \frac{k_BT}{\hbar\omega}$
Lennard-Jones Taylor series
First 5 terms
\[ V(x)/\varepsilon = -1 + 72(x-1)^2/2! - 1512(x-1)^3/3! + 20664(x-1)^4/4! \]

Level spacing in the L-J potential will diminish as n increases. Compute this by perturbation theory. Small parameter: \( \hbar \omega / \varepsilon \) or \( k_B T / \varepsilon \)
Quantum perturbation theory – simpler than classical?

\[ \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 \]

\[ \mathcal{H}_0 = \frac{p^2}{2M} + \frac{1}{2!}V_2x^2 \] where \( V_2 \) is the spring constant \( k \)

\[ \mathcal{H}_1 = \frac{1}{3!}V_3x^3 + \frac{1}{4!}V_4x^4 \] where \( V_3 \) and \( V_4 \) are anharmonic coefficients.

\[ x = \sqrt{\frac{\hbar}{2M\omega}}(a + a^\dagger) \]

\[ p = \frac{1}{i\sqrt{\frac{\hbar M\omega}{2}}}(a - a^\dagger) \]

Operator \( x \) connects \( |n\rangle \) only to \( |n \pm 1\rangle \).
Operator \( x^2 \) connects \( |n\rangle \) only to \( |n\rangle \) and \( |n \pm 2\rangle \).
Operator \( x^3 \) connects \( |n\rangle \) only to \( |n \pm 1\rangle \) and \( |n \pm 3\rangle \).
Operator \( x^4 \) connects \( |n\rangle \) only to \( |n\rangle \) and \( |n \pm 2\rangle \) and \( |n \pm 4\rangle \).

Energy level shift \( \Delta E_n = E'_n - E_n \).

\[ \Delta E_n = \langle n | (V_4x^4/4!) | n \rangle + \sum_{n'} \frac{|\langle n'| (V_3x^3/3!) | n \rangle|^2}{(n - n')\hbar \omega} \]
Landau & Lifshitz, *Quantum Mechanics*, sec 38, problem 3

\[
E_n - E_{n0} = \Delta E_n = \left( \frac{V_4}{4!} \right) \left( \frac{\hbar}{2M\omega} \right)^2 3(2n^2 + 2n + 1) - \left( \frac{V_3}{3!} \right)^2 \frac{1}{\hbar\omega} \left( \frac{\hbar}{2M\omega} \right)^3 (30n^2 + 30n + 11)
\]

Use Lennard-Jones values for \( V_3, V_4, \) and \( M\omega^2 = V_2. \)

\[
\Delta E_n = \frac{7}{384} \frac{(\hbar\omega)^2}{\epsilon} \left[ \frac{41}{3} \left( n^2 + n + \frac{1}{2} \right) - 35 \left( n^2 + n + \frac{11}{30} \right) \right]
\]

Shift of ground state level \( \Delta E_0 = -\frac{7}{64} \frac{(\hbar\omega)^2}{\epsilon}. \)

\[
\frac{\Delta E_0}{\hbar\omega} = -\frac{7}{64} \left( \frac{\hbar\omega}{\epsilon} \right)
\]

Shift of spacing of \( n^{\text{th}} \) level \( = \frac{\Delta E_{n+1} - \Delta E_{n-1}}{2} = -\frac{7}{9} \frac{(\hbar\omega)^2}{\epsilon} \left( n + \frac{1}{2} \right) \)

Relative shift of level spacing, for thermal average level \( \bar{n}: \)

\[
\frac{\delta \omega_{\bar{n}}}{\omega} = -\frac{7}{9} \frac{k_B T}{\epsilon}
\]

Predicted oscillator frequency shift
3: $\text{CO}_2$ molecular vibrations

Molecular structure of Carbon Dioxide

The asymmetric stretch mode

The bending mode

The symmetric stretch mode

The first few vibrational energy levels of the CO2 molecule

Derek Kverno, Davidson College
Neglect bending – consider only one dimensional motions. Choose the origin at the center of mass; define displacement coordinates $u_i$

\[ u_1 = x_1 + a, \quad u_2 = x_2, \quad u_3 = x_3 - a, \quad \langle u_1 \rangle = \langle u_2 \rangle = \langle u_3 \rangle = 0 \]

$\alpha = \text{equilibrium C - O distance}; \text{mass } m_1 = m_3.$

\[ H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{p_3^2}{2m_3} + V(u_1,u_2,u_3) \]

Approximate $V$ by nearest neighbor central spring model.

\[ V(u_1,u_2,u_3) = \frac{1}{2}k(u_1 - u_2)^2 + \frac{1}{2}k(u_3 - u_2)^2 \]

Newtonian equations of motion

\[ m_1 \ddot{u}_1 = -\frac{\partial V}{\partial u_1} = -k(u_1 - u_2) \]

\[ m_2 \ddot{u}_2 = -\frac{\partial V}{\partial u_2} = -k(u_2 - u_1) - k(u_2 - u_3) \]

\[ m_3 \ddot{u}_3 = -\frac{\partial V}{\partial u_3} = -k(u_3 - u_2) \]
Matrix form of equation of motion (note: \( m_1 = m_3 \) for \( CO_2 \))

\[
-\frac{d^2}{dt^2} \begin{pmatrix}
  m_1 & 0 & 0 \\
  0 & m_2 & 0 \\
  0 & 0 & m_3
\end{pmatrix}
\begin{pmatrix}
  u_1 \\
  u_2 \\
  u_3
\end{pmatrix}
= \begin{pmatrix}
  k & -k & 0 \\
  -k & 2k & -k \\
  0 & -k & k
\end{pmatrix}
\begin{pmatrix}
  u_1 \\
  u_2 \\
  u_3
\end{pmatrix}
\]

Abstract (Dirac) notation for matrix and vector

\[
-\frac{d^2}{dt^2} \hat{M} \left| u \right> \Rightarrow \hat{K} \left| u \right>
\]

where

\[
\left| u \right> = \begin{pmatrix}
  u_1 \\
  u_2 \\
  u_3
\end{pmatrix}
\]

and \( \hat{M} \) is the (diagonal) mass matrix

and

\[
\hat{K}
\]

is the (real symmetric) force constant matrix

Define

\[
\left| s \right> = \frac{1}{M} \left| u \right>
\]

or

\[
\begin{pmatrix}
  s_1 \\
  s_2 \\
  s_3
\end{pmatrix}
= \begin{pmatrix}
  u_1 \sqrt{m_1} \\
  u_2 \sqrt{m_2} \\
  u_3 \sqrt{m_3}
\end{pmatrix}
\]

mass-weighted coordinates
The Newtonian equation of motion becomes

$$-\frac{d^2}{dt^2} |s> = \hat{D} |s>$$

where $\hat{D}$ is the (real-symmetric) “dynamical matrix.”

$$\hat{D} = M^{-\frac{1}{2}} K M^{-\frac{1}{2}} = \begin{pmatrix}
\frac{k}{m_1} & -\frac{k}{\sqrt{m_1 m_2}} & 0 \\
-\frac{k}{\sqrt{m_1 m_2}} & 2\frac{k}{m_2} & -\frac{k}{\sqrt{m_2 m_3}} \\
0 & -\frac{k}{\sqrt{m_2 m_3}} & \frac{k}{m_3}
\end{pmatrix}$$

$\hat{K}$ and $\hat{D}$ are both “non-negative.” This follows from the fact that

$$\frac{1}{2} <u|\hat{K}|u> = V(u_1, u_2, u_3)$$

and the potential energy of a stable oscillator is never negative.

$\hat{D}$ has non-negative eigenvalues (call them $\omega_i^2, i=1,2,3$) and orthonormal eigenvectors $|i>$

$$\hat{D} |i> = \omega_i^2 |i>$$
There is always a “null eigenvector,”

\[
\hat{D} |0> = \begin{pmatrix}
\frac{k}{m_1} & -\frac{k}{\sqrt{m_1 m_2}} & 0 \\
-k \sqrt{m_1 m_2} & 2 \frac{k}{m_2} & -\frac{k}{\sqrt{m_2 m_3}} \\
0 & -\frac{k}{\sqrt{m_2 m_3}} & \frac{k}{m_3}
\end{pmatrix} |0> = 0 \quad \text{where} \quad |0> = \begin{pmatrix}
\sqrt{m_1} \\
\sqrt{m_2} \\
\sqrt{m_3}
\end{pmatrix}
\]

The vector \(|s>=|0>\) corresponds to \(|u>=\begin{pmatrix}c \\ c \\ c\end{pmatrix}\) a uniform translation - all atoms have the same displacement.

Because \(m_1=m_3\), the matrix \(D\) has extra symmetry which allows eigenvectors to be found by “guessing.”

\(|1>=\begin{pmatrix}1 \\ 0 \\ -1\end{pmatrix}\) is an eigenvector with eigenvalue \(\omega_1^2=k/m_1\) symmetric stretch

prediction: \(\omega_2/\omega_1=\sqrt{1+2m_1/m_2}\) =1.9 (1.7 is found experimentally.)
What is special about eigenvectors $|i\rangle$ of $D$?

$|s\rangle = A\cos(\omega t + \varphi)|i\rangle$ is a solution of Newton’s laws provided $\omega$ is chosen as the eigenvalue $\omega_i$. It is a “stationary solution” or “normal mode.” The “pattern” of oscillation is fixed in time.

The normal modes are “complete.” All solutions of Newton’s laws can be built from them. They also generate corresponding quantum results, i.e. solutions of the Schrödinger equation.

A simple way to designate a complete set of stationary (many body) quantum states is $|n_1, n_2, ..., n_i, ...\rangle$. This specifies, for each normal mode, the integer level $n_i$ of excitation of the $i^{th}$ mode. **Reinterpretation:**

Instead of the excitation level of a normal mode, we regard $n_i$ as its “occupancy.” That is, we ask how many quanta of vibration are “in the $i^{th}$ mode.”

The different normal modes are “independent” (in Harmonic approximation.) All extensive thermodynamic functions are sums over the thermodynamics of the independent normal modes.

There are $3N$ normal modes for a bound system of $N$ atoms in $d=3$ (actually $3N-6$ when we separate uniform translations and rotations.)
A finite system can’t be truly periodic. Solution - Born-von Karman (periodic) boundary conditions. Attach periodic replicas which copy the N-atom finite system.

\[ V = \frac{1}{2}k(u_1-u_2)^2 + \frac{1}{2}k(u_2-u_3)^2 + \ldots + \frac{1}{2}k(u_N-u_1)^2 \]

Unequal masses are treated as in CO₂ - Homework!
Translation operators $\hat{T}_n$

$$\begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{pmatrix} = \begin{pmatrix} u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \\ u_1 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{pmatrix}$$

Multiplication rules: $T_i$ form an Abelian group

$T_1^2 = T_2, \quad T_1^N = T_N = T_0 = 1$

$T_1^{-1} = T_{-1}, \quad T_m T_n = T_{m+n}$

$T_m T_n = T_n T_m$

Newton equation of motion in matrix form using translation matrices

$$-\frac{d^2}{dt^2} |u> = \frac{k}{m} \left( 2\hat{T}_0 - \hat{T}_1 - \hat{T}_{-1} \right) |u> = \hat{D} |u>$$

Dynamical matrix $\mathbf{D}$ is built from translation matrices $\mathbf{T}$, and commutes with them. Therefore, we can build eigenstates of the dynamical matrix using eigenstates of translations. These are traveling waves.
Look for eigenstates of $T_1$

If $|\phi\rangle$ is an eigenstate of $T_1$ with eigenvalue $e^{i\phi}$, then it is an eigenstate of $T_2$ with eigenvalue $e^{i2\phi}$, etc.

Provided $e^{iN\phi}=1$ (here $N=6$)

$e^{i\phi}$ must be one of the $N$ roots of unity. There are $N$ such roots, on the unit circle.

$\phi = \frac{2\pi m}{N} = \frac{2\pi ma}{Na = L} \equiv (ka)$

$k \equiv \frac{2\pi m}{L} = \frac{2\pi}{\lambda}$

Mathematical meaning of the wave vector $k$ - the eigenvalue of $T_1 = T(a)$ is $e^{ika}$.

Therefore, $k$ and $k+2\pi/a$ have exactly the same meaning.

Warning - notation! $k$ is used for wave vector and for spring constant!
Bloch's Theorem

Operators like $\mathcal{H}$ and $D$ for a periodic system commute with the translations. Therefore, we can choose eigenstates of $\mathcal{H}$ and $D$ to be simultaneously eigenstates of all $T_i$. These eigenstates are labeled by their wavevector $\mathbf{k}$.

$$\hat{T}_1 | k \rangle = e^{ika} | k \rangle \quad \hat{D} = \frac{k}{m} (2\hat{T}_0 - \hat{T}_1 - \hat{T}_{-1}) \rightarrow \frac{k}{m} (2 - e^{ika} - e^{-ika})$$

$$\omega^2(k) = \text{eigenvalue of } D = \frac{k}{m} (2 - 2 \cos(ka)) = 4 \frac{k}{m} \sin^2(ka/2)$$

$$\omega(k) = \omega_{\text{max}} \left| \sin(ka/2) \right|$$

$$\omega_{\text{max}} = 2 \sqrt{\frac{k}{m}}$$

Continuum ("Debye") limit: propagating sound waves $\omega = v|k|$
1. There are exactly $N$ k-vectors $\vec{k}$ which label the inequivalent eigenvectors $|k\rangle$ of $T$. These $N$ k-vectors lie in the Brillouin zone.

2. Bloch states $|k\rangle$ with inequivalent $\vec{k}$'s are orthogonal. Norm = 1. Thus $\langle k'|k\rangle=(1/N)\sum_R e^{i(k-k')R} = \delta(k,k') \text{ modulo } G$

3. The states $|k\rangle$ are complete in the N-dimensional space:
$$\sum_k |k\rangle\langle k| = (1/N)\sum_k e^{i(k-R'k')} = \delta(R-R') \text{ [R runs over the discrete lattice points.] }$$

4. Sums become integrals:
$$\sum_k f(k) = \left(\frac{L}{2\pi}\right)^d \int_{\text{BZ}} d^d k \ f(k)$$

$\vec{k}$
Same linear chain, lattice constant $a$, spring constant $\beta$, alternating masses $M$ and $m$.

\[
\begin{align*}
    m \frac{\partial^2 U_{2n}}{\partial t^2} &= \beta (U_{2n+1} - 2U_{2n} + U_{2n-1}) \\
    M \frac{\partial^2 U_{2n+1}}{\partial t^2} &= \beta (U_{2n+2} - 2U_{2n+1} + U_{2n}) \\
    U_{2n} &= A \exp[i(2n\alpha \pm \omega t)] \\
    U_{2n+1} &= B \exp[i((2n+1)\alpha \pm \omega t)]
\end{align*}
\]

\[
\omega^2 = \beta \left(\frac{1}{m} + \frac{1}{M}\right) = \beta \sqrt{\left(\frac{1}{m} + \frac{1}{M}\right)^2 - \frac{4\sin^2 \kappa a}{Mn}}
\]

Phonon dispersion in tungsten metal

"first principles" calculation
Density-functional theory
C. Bungaro, thesis, SISSA, 1995
(with Baroni and Gironcoli)
simple cubic Brillouin zone

The Brillouin zone (BZ) is the unit cell of “reciprocal space.”

Primitive vectors of the reciprocal lattice:
- \( h_1 = A = (2\pi/a)(100) \)
- \( h_2 = B = (2\pi/a)(010) \)
- \( h_3 = C = (2\pi/a)(001) \)

Multiple ways to define shape of unit cell.
- Wigner-Seitz Construction works for direct or reciprocal lattice.

\( X = (\pi/a)(100) \) or similar