Prof Fink's Notes (Fall 2006): The Hamiltonian approach to classical mechanics and the analysis of lattice vibrations

Introduction:

While this course is primarily focused on electronic structure and it's relation to EPM properties it is useful to briefly review the Hamiltonian or *energetics* approach to classical mechanics. We will begin with an analysis of lattice vibrations which provide a mechanism for energy storage and contribute to the heat capacity. Related to this model is the "Law of Dulong and Petit" which predicts that at high temperatures each ion in a solid contributes $3k_B$ (~25J/mol K). Lattice vibrations also play a key role in limiting the electrical conductivity in metals, mediating heat conduction and also enable optical transitions in indirect band semiconductors. Lattice vibrations also determine the speed of sound in materials.

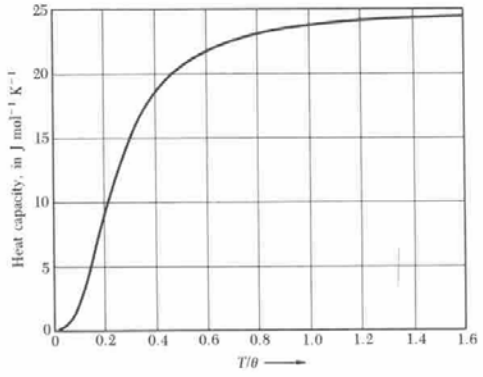


Figure 7 Heat capacity C_V of a solid, according to the Debye approximation. The vertical scale is in J mol^{-1} K^{-1}. The horizontal scale is the temperature normalized to the Debye temperature θ. The region of the T^3 law is below 0.1θ. The asymptotic value at high values of T/θ is 24.943 J mol^{-1} deg^{-1}.

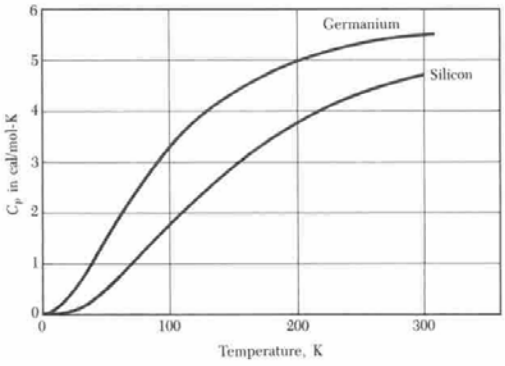


Figure 8 Heat capacity of silicon and germanium. Note the decrease at low temperatures. To convert a value in cal/mol-K to J/mol-K, multiply by 4.186.

The structure of classical mechanics: states, hamiltonians and time evolution

Our analysis of a classical collection of particles in a region of space where a potential energy can be defined as a function of the spatial coordinates also known as a potential field follow a number of steps

I. System

Here the physical system is defined. The individual masses are identified as well as the potential energy. Also included in this section is the definition of a coordinate system that captures the degrees of freedom of the system.

II. The state

The state of a classical system at a particular time t_0 typically determined by the position and momentum variables $x(t_0)$ and $p(t_0)$.

III. The Hamiltonian

All physical quantities of the system (energy, angular momentum) can be expressed as functions of these variables. For example: the total energy of the system is determined by its classical Hamiltonian which can be usually defined as,

$$H(x,p,t)=\frac{p^2}{2m}+V(x,t)$$

IV. Time evolution of the state

Once the state $\left(x(t),p(t)\right)$ is known at a particular time t_0 the state of the system at any other time t is determined completely by the equations of motion which are also known as Hamilton's equations.

$$\frac{\partial H(x,p,t)}{\partial p_i}=\frac{dx_i}{dt}$$
$$\frac{\partial H(x,p,t)}{\partial x_i}=-\frac{dp_i}{dt}$$

the complete set of $\left(x(t),p(t)\right)$ is called the *trajectory* of the system. To solve this system of coupled first order differential equations it is necessary to specify the initial conditions.

Example I: mass in a gravitational field

The system consists of a single mass m=1kg which is released at t=0 from a height of 1m above the floor the state of the system at t=0 is $\left(x(t=0)=1,p(t=0)=0\right)$ the total energy is given by the Hamiltonian,

$$H(x,p,t)=\frac{p^2}{2m}+mgx=1[kg]9.8\left[\frac{m}{s^2}\right]1[m]=9.8[J]=6.11\times10^{19}[eV]$$

The time evolution of the state is given by,

$$\frac{\partial H(x,p,t)}{\partial p} = \frac{p}{m} = \frac{dx}{dt}$$
$$\frac{\partial H(x,p,t)}{\partial x} = mg = -\frac{dp}{dt}$$

two coupled first order differential equations, solve them by directly integrating the second equation with respect to time….

$$-\int_0^t mg\,dt = \int_{p(0)}^{p(t)} dp$$
$$\rightarrow p(0) - mgt = p(t)$$

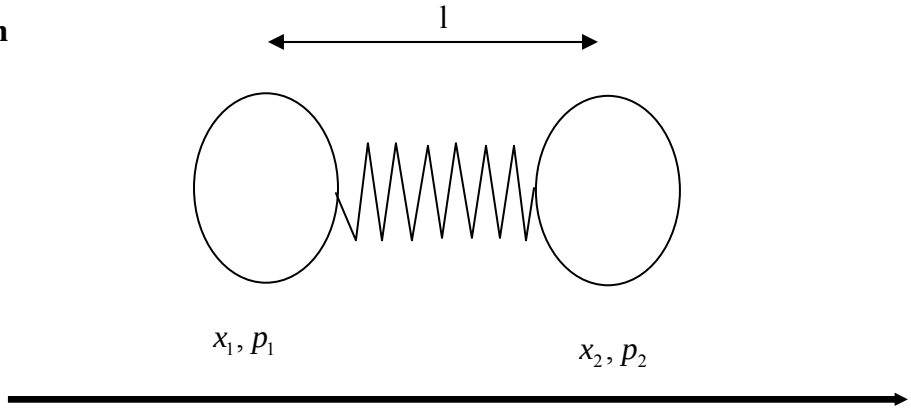
then we substitute the p(t) found into the first equation…

$$\int_0^t \frac{p(t)}{m}\,dt = \int_{x(0)}^{x(t)} dx$$
$$\int_0^t \frac{p(0) - mgt}{m}\,dt = \int_{x(0)}^{x(t)} dx$$
$$x(0) + \frac{p(0)}{m}t - \frac{g}{2}t^2 = x(t)$$

and finally the initial conditions are used (i.e. x(0) and p(0)) to obtain the trajectory.

Example II: 1D Diatomic molecule

I. The system



II. The Hamiltonian

$$H\left(x_1, p_1; x_2, p_2\right) = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{K}{2}\left(x_2 - x_1 - l\right)^2$$

k is the spring constant and l is the equilibrium position of the spring (i.e. at that distance the spring is not exerting any force on the masses)

III. The equations of motion

$$\frac{\partial H\left(x_1, p_1, x_2, p_2; t\right)}{\partial p_1} = \frac{p_1}{m} = \frac{dx_1}{dt}$$

$$\frac{\partial H\left(x_1, p_1, x_2, p_2; t\right)}{\partial x_1} = -\frac{dp_1}{dt} \rightarrow -K\left(x_2 - x_1 - l\right) = -\frac{dp_1}{dt}$$

$$\frac{\partial H\left(x_1, p_1, x_2, p_2; t\right)}{\partial p_2} = \frac{p_2}{m} = \frac{dx_2}{dt}$$

$$\frac{\partial H\left(x_1, p_1, x_2, p_2; t\right)}{\partial x_2} = -\frac{dp_2}{dt} \rightarrow K\left(x_2 - x_1 - l\right) = -\frac{dp_2}{dt}$$

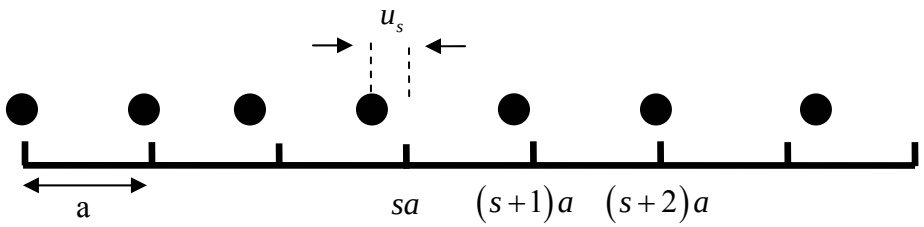
$$\dot{x}_1 = \frac{p_1}{m},\ \dot{x}_2 = \frac{p_2}{m},\ \dot{p}_1 = K\left(x_2 - x_1 - l\right),\ \dot{p}_2 = -K\left(x_2 - x_1 - l\right)$$

these coupled first order equations can be solved by generating uncoupled second order equations.

Example III: Longitudinal vibrations of a one dimensional monoatomic lattice (can be applied to cubic crystals with a mono-atomic basis)

I. The system

Consists of ions located on a lattice defined by a lattice vector x=sa. The ions are assumed to be deviating from their respective lattice points by a distance u.which is taken to be smaller than a, which is, the lattice constant.



II. The Hamiltonian

We assume that the elastic energy is quadratic in the displacement
Write Hamiltonian for the crystal where the problem is parameterized by the coordinate s and the displacement vector $[u_s]$

$$H = \sum_s \frac{{p_s}^2}{2M} + \frac{1}{2} K \sum_s \left(u_s - u_{s+1}\right)^2$$

III. Deriving the equations of motion

Through the application of Hamilton's equations we derive the equations of motion:

$$\frac{\partial H}{\partial u_s} = -\frac{dp_s}{dt}$$

$$\frac{\partial H}{\partial p_s} = \frac{du_s}{dt}$$

Focus on the terms in the Hamiltonian that contain u_s and p_s

$$H_s = \frac{{p_s}^2}{2M} + \frac{1}{2} K \left(u_s - u_{s+1}\right)^2 + \frac{1}{2} K \left(u_{s-1} - u_s\right)^2 + \ldots +$$

And obtain

$$M \frac{d^2 u_s}{dt^2} = K \left(u_{s+1} + u_{s-1} - 2u_s\right)$$

Look for solutions that have a time dependence of the form, and substitute back in the above equation to obtain a *difference* equation:

$$u_s \propto e^{-i\omega t} \rightarrow \frac{d^2 u_s}{dt^2} = -\omega^2 u_s$$

$$\rightarrow -M\omega^2 u_s = K \left(u_{s+1} + u_{s-1} - 2u_s\right)$$

This difference equation has solution of the form:

$$u_{s\pm1} = ue^{i(s\pm1)ka}$$

where *a* is the lattice constant and k is called the wavevector.

The solution per atom s can also be written as:

$$u_k(s,t) = ue^{iksa-i\omega t}$$

$$-M\omega^2 e^{iska} = K\left(e^{i(s+1)ka} + e^{i(s-1)ka} - 2e^{iska}\right)$$

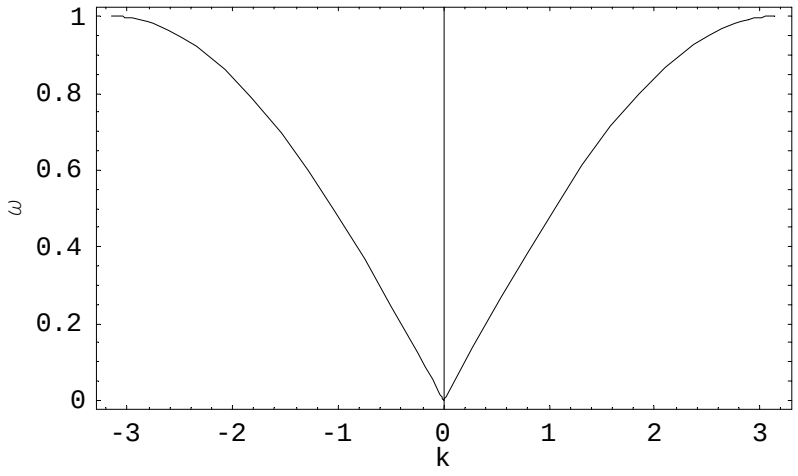
$$\rightarrow -M\omega^2 = K\left(e^{ika} + e^{-ika} - 2\right)$$

$$\rightarrow \omega^2(k) = \frac{2K}{M}(1-\cos ka)$$

$$\rightarrow \omega(k) = \sqrt{\frac{4K}{M}}\left|\sin\frac{ka}{2}\right|$$

Dispersion relations

The last equation defines the dispersion relation which is a periodic function in k



The dispersion relation constitutes a graphical representation of the independent solutions. Given a vector of initial displacements $\left[u(0)\right]$ and initial velocities $\left[\dot{u}(0)\right]$, *k* and ω define a solution.

Physical characteristics of the solutions:

1. The ratio of two adjacent displacements is:
   $\frac{u_{s+1}}{u_s} = \frac{ue^{ik(s+1)a}}{ue^{iksa}} = e^{ika}$ which indicates that a solution involving k and a solution that has a k'=k+n2π/a are equivalent.
2. Unique solutions only for those values of k that are restricted to the first BZ:
   $-\frac{\pi}{a} \le k \le \frac{\pi}{a}$
3. Phase velocity: $c = \frac{\omega}{k}$ and group velocity: $v_g = \frac{d\omega}{dk} = \sqrt{\frac{Ka^2}{M}} \cos\frac{ka}{2}$
4. Standing waves at the edge of the Brillouin zone for solutions where k satisfies:
   $k = \pm\frac{\pi}{a}$. Adjacent atoms move in opposite directions the wave is not propagating (group velocity is 0).

> This is the same condition that is satisfied when you get the so called Bragg reflections in optics (or x-ray diffraction). Recall the condition for Bragg diffraction:
>
> $$2d\sin\theta = n\lambda$$
>
> $$\theta = \frac{\pi}{2},\ d = a,\ \text{n=1} \rightarrow \lambda\text{=2a}$$
>
> k is the wavevector and is related to the wavelength by:
>
> $$k = \frac{2\pi}{\lambda}$$
>
> We just saw from the analysis above that we get standing waves at
>
> $$k_{standing} = \pm\frac{\pi}{a}$$
>
> which is identical the Bragg condition.

5. Long wavelength limit occurs when *ka*<<1. Under these conditions the dispersion relations can be expanded in a Taylor series:
   $$\omega^2(k) = \frac{2K}{M}(1-\cos ka)$$
   $$\cos ka = 1 - \frac{(ka)^2}{2} + O\left((ka)^4\right)$$
   $$\omega = \sqrt{\frac{K}{M}}ka$$
   and the velocity of sound $v_g = \frac{d\omega}{dk} = \sqrt{\frac{K}{M}}a$ is independent of frequency.

Longitudinal vibrations of a one dimensional diatomic lattice (cubic crystals with diatomic basis)

Degrees of freedom:

When a crystal has two atoms or more per primitive basis, such as Rocksalt structure of NaCl (FCC with two atom basis), Diamond structure (FCC with two atom basis) of Si, Ge, diamond carbon or α-Sn each polarization mode develops two branches known as acoustic and optical branches. If there are p atoms in the primitive cell, there are 3p branches to the dispersion relations: 3 acoustical branches and 3p-3 optical branches. We will focus for the purpose of this discussion on a simplified 1D model similar to the one discussed above:

I. The system

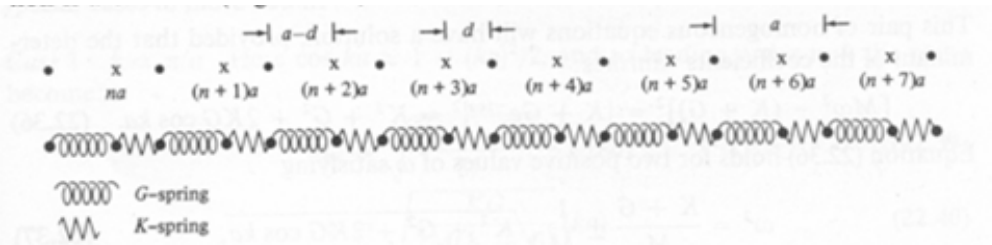


Figure 22.9
The diatomic linear chain of identical atoms, connected by springs of alternating strengths.

II. The Hamiltonian

$$H=\sum_s \frac{{p_{1s}}^2}{2M}+\sum_s \frac{{p_{2s}}^2}{2M}+\frac{1}{2}K\sum_s\left(u_{1s}-u_{2s}\right)^2+\frac{1}{2}G\sum_s\left(u_{2s}-u_{1s+1}\right)^2$$

III. Equations of motion

$$M\frac{d^2u_{1,s}}{dt^2}=K\left(u_{2,s}-u_{1,s}\right)+G\left(u_{2,s-1}-u_{1,s}\right)$$

$$M\frac{d^2u_{2,s}}{dt^2}=K\left(u_{1,s}-u_{2,s}\right)+G\left(u_{1,s+1}-u_{2,s}\right)$$

IV. Solutions

$$u_{1s}=u_1e^{iksa}e^{-i\omega t},\ u_{2s}=u_2e^{iksa}e^{-i\omega t}$$

V. Dispersion relations

$$\left(M\omega^2-\left(K+G\right)\right)u_1+\left(K+Ge^{-ika}\right)u_2=0$$

$$\left(K+Ge^{ika}\right)u_1+\left(M\omega^2-\left(K+G\right)\right)u_2=0$$

The homogenous linear equations have a solution only if the determinant of the coefficients is zero:

$$\begin{vmatrix} \left(M\omega^2 - \left(K+G\right)\right) & \left(K+Ge^{-ika}\right) \\ \left(K+Ge^{ika}\right) & \left(M\omega^2 - \left(K+G\right)\right) \end{vmatrix} = 0$$

with solutions:

$$\omega^2 = \frac{K+G}{M} \pm \frac{1}{M}\sqrt{K^2+G^2+2KG\cos ka}$$

$$\frac{u_1}{u_2} = \mp \frac{K+Ge^{-ika}}{\left|K+Ge^{ika}\right|}$$

for each k there are two solutions which are called the two branches of the dispersion curves.

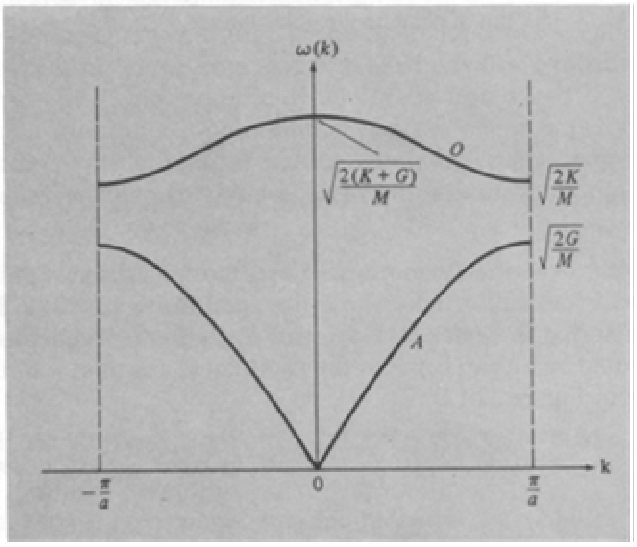


Figure 22.10
Dispersion relation for the diatomic linear chain. The lower branch is the acoustic branch and has the same structure as the single branch present in the monatomic case (Figure 22.8). In addition, there is now an optical branch (upper branch.)

Let us examine the following limiting cases of the dispersion relations:

Case I: Long wavelength $ka << \pi$

$$\omega^2 \cong 2\left(\frac{K+G}{M}\right), u_1 = -u_2 \qquad \left(\text{Optical branch}\right)$$

$$\omega^2 \cong \frac{KG}{2M\left(K+G\right)}\mathrm{k}^2\mathrm{a}^2, u_1 = u_2 \qquad \left(\text{Acoustic branch}\right)$$

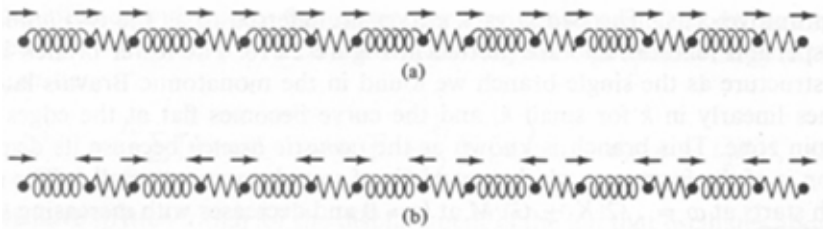


Figure 22.11
The long wavelength acoustic (a) and optical (b) modes in the diatomic linear chain. The primitive cell contains the two ions joined by the *K*-spring, represented by a jagged line. In both cases the motion of every primitive cell is identical, but in the acoustic mode the ions within a cell move together, while they move 180° out of phase in the optical mode.

Case II: $ka = \pi$

$$\omega^2\left(k = \frac{\pi}{a}\right) = \frac{2K}{M}, u_1 = -u_2$$

$$\omega^2\left(k = \frac{\pi}{a}\right) = \frac{2G}{M}, u_1 = u_2$$

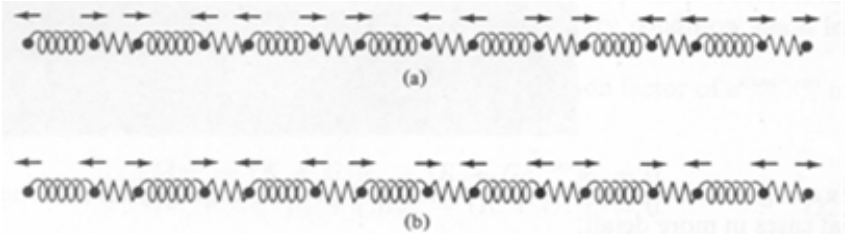


Figure 22.12
The acoustic (a) and optical (b) modes of the diatomic linear chain, when $k = \pm\pi/a$, at the edges of the Brillouin zone. Now the motion changes by 180° from cell to cell. However, as in Figure 22.11, the ions within each cell move in phase in the acoustic mode, and 180° out of phase in the optical mode. Note that if the *K*- and *G*-springs were identical the motion would be the same in both cases. This is why the two branches become degenerate at the edges of the zone when $K = G$.

Case III: K>>G

$$\omega^2 \cong \frac{2K}{M}, u_1 = -u_2$$

$$\omega^2 \cong \frac{2G}{M}\left|\sin\frac{ka}{2}\right|, u_1 = u_2$$

The optical branch now has a frequency which is k independent and is approximately equal to that of the frequency of vibration of a diatomic molecule. This leads to an additional insight into the physical interpretation of the optical branch and the distinction between it and the acoustic branch. Essentially, this branch is a band of frequencies which results from the broadening associated with the coupling between the individual oscillators. The motion thus originates from the diatomic motion. In the acoustic mode the ions in a cell are moving in the same direction and thus the motion is essentially a collective motion.

Spring Constants and Young's Modulus (a simple derivation)

The harmonic analysis described above assumed elastic energy that is proportional to the displacement squared which resulted in a force proportional to the displacement and opposite to it in direction (restoring force):

$$potential\ energy = \frac{K}{2}u^2$$

$$F = -Ku$$

K is related to the bond stiffness. If one applies a force to a cross section of a solid, N bonds are stretched. The force needed to be applied per unit area is called the stress:

$$\sigma = NK\underbrace{\left(x - x_0\right)}_{\equiv u}$$

N is the number of bonds per unit area $N = \frac{1}{x_0^2}$

$$\sigma = \underbrace{\frac{K}{x_0}}_{E}\underbrace{\frac{\left(x - x_0\right)}{x_0}}_{\equiv \varepsilon}$$

Which relates (in an oversimplified way) the spring constant (or bond stiffness) to the Elastic moduli E which is the macroscopically measured quantity.

Bond type	S_o ($N m^{-1}$)	E(GPa); from eqn. (6.5) (with $r_0 = 2.5 \times 10^{-10}$ m)
Covalent, e.g. C–C	50–180	200–1000
Metallic, e.g. Cu–Cu	15–75	60–300
Ionic, e.g. Na–Cl	8–24	32–96
H-bond, e.g. H_2O–H_2O	2–3	8–12
Van der Waals, e.g. Polymers	0.5–1	2–4

One of the best methods for measuring Young's modulus of materials is through the velocity of sound. For the velocity of a longitudinal wave in the [100] direction of a cubic crystal we have:

$$v_l = \left(\frac{E}{\rho}\right)^{1/2} = \left(\frac{C_{11}}{\rho}\right)^{1/2}$$

where C_{11} is one of the three independent elastic stiffness coefficients for a cubic crystal. One typically attaches a piezoelectric crystal to one end and measures the time it takes the excitation to reach the other end.