Blackbody radiation (photons)

and

Lattice vibrations (phonons)

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References:

Baierlain, Thermal Physics, chapter 6

Salinas, chapters 10 and 11.

Landau, chapter 5 (Sec 63) and chapter 6

For phonons, the best reference is Ashcroft and Mermin, chapters 22 and 23.

Photons in a box

A photon is completely characterized by its wave vector k and its polarization $\alpha = 1, 2$ (You can take 1 for x-polarized and 2 for y-polarized. Or you can use circular polarization, it makes no difference). The dispersion relation for photons is

$$\omega_k = c |k| \tag{1}$$

It is independent of the polarization.

Now suppose you have a bunch of photons in a box. For each state (k, α) we may have $m(k, \alpha)$ photons. The energy of each photon is $h\nu = \hbar \omega$. Thus the total energy will be

$$E = \sum_{k, \alpha} \hbar \omega_{k} \, m(k, \alpha) \tag{2}$$

the values of $m(k, \alpha)$ will depend on the conditions that you set up your electromagnetic field. Nowadays people can construct experiments where the cavity (ie, the "box") has just one photon of one wave vector. We would write that as

$$m(k, \alpha) = \begin{cases} 1 & k = k_0, \ \alpha = \alpha_0 \\ 0 & \text{otherwise} \end{cases}$$

of course, you can imagine building cavities with all sorts of photon configurations. But here we will be interested in <u>thermal configurations</u>

we are going to assume that the walls of our cavity are in thermal equilibrium at a given temperature T. Consequently, the $n(k,\alpha)$ will become random variables: there will be a continuous creation and annihilation of photons due to the thermal agittation of the atoms in the wall.

What we want to ask, therefore, is what is the average photon number $\langle n(k,\alpha)\rangle$? Well this is easy: this problem is mathematically analogous to the quantum harmonic oscillator.

Recall

$$E_J = \hbar \omega M \qquad\qquad M = 0, 1, 2, 3, \cdots$$

$$\Rightarrow \quad z_J = \sum_{M=0}^{\infty} e^{-\beta\hbar\omega M} = \frac{1}{1 - e^{-\beta\hbar\omega}} \tag{3}$$

$$\tag{4}$$

$$\langle M \rangle = \frac{1}{e^{\beta\hbar\omega} - 1}$$

thus, the average occupation number $\langle n(k,\alpha)\rangle$ will be

$$\tag{5}$$

$$\langle n(k,\alpha)\rangle = \frac{1}{e^{\beta\hbar\omega_k} - 1}$$

we may now write all thermodynamic quantities we want. For instance, the internal energy will be

$$\tag{6}$$

$$U = \sum_{k,\alpha} \hbar\omega_k \langle n(k,\alpha)\rangle = \sum_{k,\alpha} \frac{\hbar\omega_k}{e^{\beta\hbar\omega_k} - 1}$$

We can also go beyond: the total number of photons will be

$$N = \sum_{k,\alpha} \langle M(k,\alpha) \rangle = \sum_{k,\alpha} \frac{1}{e^{\beta\hbar\omega_k} - 1} \tag{7}$$

The partition function will be a product of the individual partition functions

$$Z = \prod_{k,\alpha} \left[\frac{1}{1 - e^{-\beta\hbar\omega_k}} \right] \tag{8}$$

Thus, the free energy will be a sum

$$F = -k_B T \ln Z = k_B T \sum_{k,\alpha} \ln(1 - e^{\beta\hbar\omega_k}) \tag{9}$$

If we have F, then we can compute the entropy as

$$S = \frac{U - F}{T} \tag{10}$$

and even the pressure as

$$P = -\frac{\partial F}{\partial V} \tag{11}$$

This is the <u>radiation pressure</u>: Yes, radiation also exerts a pressure

The density of states for electromagnetic radiation

If you look back you will see that all thermodynamic quantities have the form

$$\sum_{k,\alpha} f(\omega_k)$$

where f is an arbitrary function. It is convenient to convert this into an integral:

$$\sum_{k,\alpha} f(\omega_k) \longrightarrow \int_0^\infty d\omega \, g(\omega) f(\omega) \qquad (12)$$

the quantity $g(\omega)$ is called the density of states (DOS). the procedure to find it is similar to the one we used when we discussed the ideal gas.

First we note that ω_k does not depend on α (the polarization) so

$$\sum_{k,\alpha} f(\omega_k) = 2 \sum_k f(\omega_k) \qquad (13)$$

Next, we note that since the photons are in a box, the k's are quantized as

$$k_i = \frac{2\pi M_i}{L}, \quad M_i = 0, \pm 1, \pm 2, \cdots \qquad (14)$$

[k's are always quantized like this]. Thus $\Delta k_i = \frac{2\pi}{L}$

we use this to conveniently insert a "1":

$$2 \sum_{\vec{k}} f(\omega_{\vec{k}}) = 2 \left(\frac{L}{2\pi}\right)^3 \sum_{\vec{k}} \Delta k_x \, \Delta k_y \, \Delta k_z \, f(\omega_{\vec{k}})$$

this now has the form of a Riemann sum, so we may write $(V=L^3)$

$$2 \sum_{\vec{k}} f(\omega_{\vec{k}}) = 2 \frac{V}{(2\pi)^3} \int d^3k \, f(\omega_{\vec{k}})$$

Now we note that $\omega_{\vec{k}} = c|\vec{k}|$ depends only on $k = |\vec{k}|$. We therefore change to spherical coordinates

$$d^3k = k^2 \, dk \, d\Omega$$

The integral over $d\Omega$ gives 4π so

$$2 \sum_{\vec{k}} f(\omega_{\vec{k}}) = 2 \frac{V}{(2\pi)^3} 4\pi \int_0^\infty dk \, k^2 f(\omega_{\vec{k}})$$

Finally, we change the integration variable from k to $\omega = ck$. We will then have

$$k^2 dk = \left(\frac{\omega}{c}\right)^2 \frac{d\omega}{c} = \frac{\omega^2 d\omega}{c^3}$$

thus

$$2 \sum_{\vec{k}} f(\vec{k}) = \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \, \omega^2 f(\omega)$$

we therefore conclude that the density of states will be

$$\boxed{g(\omega) = \frac{V}{\pi^2 c^3} \omega^2}$$

(15)

⑤

The Planck distribution

Now that we know $g(\omega)$ we are ready to compute any k-sum we want. We start with the internal energy, Eq (6):

$$U = \sum_{k,\alpha} \frac{\hbar \omega_k}{e^{\beta \hbar \omega_k} - 1} = \int_0^\infty d\omega \, g(\omega) \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \tag{16}$$

or

$$U = \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \frac{\hbar \omega^3}{e^{\beta \hbar \omega} - 1} \tag{17}$$

We will do this integral in a minute. But first I want to analyze the integrand. We may write this formula as

$$U = V \int_0^\infty d\omega \, \rho(\omega) \tag{18}$$

where

$$\boxed{\rho(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\beta \hbar \omega} - 1}} \tag{19}$$

this quantity gives an <u>energy</u> per <u>unit</u> <u>frequency</u>. It is the fraction of the total energy which has frequency ω. Eq (19) is known as the <u>Planck distribution</u>. It was proposed by Max Planck in 1900 and marks the birth of quantum mechanics.

It is more common to make plots as a function of the wavelength λ (oops! this is not the polarization

$$\omega = ck = c\frac{2\pi}{\lambda}$$

we will then have

$$d\omega = -\frac{2\pi c}{\lambda^2} d\lambda$$

so

$$\int_0^\infty d\omega\, \rho(\omega) = -2\pi c \int_\infty^0 \frac{d\lambda}{\lambda^2} \rho(\omega(\lambda)) = \int_0^\infty \frac{2\pi c\, d\lambda}{\lambda^2} \rho(\omega(\lambda))$$

Thus

$$\rho(\lambda)\, d\lambda = \rho(\omega)\, d\omega$$

and

$$\rho(\lambda) = \frac{2\pi c}{\lambda^2}\; \frac{\hbar}{\pi^2 c^3} \left(\frac{2\pi c}{\lambda}\right)^3 \frac{1}{e^{\beta \hbar c 2\pi/\lambda} - 1}$$
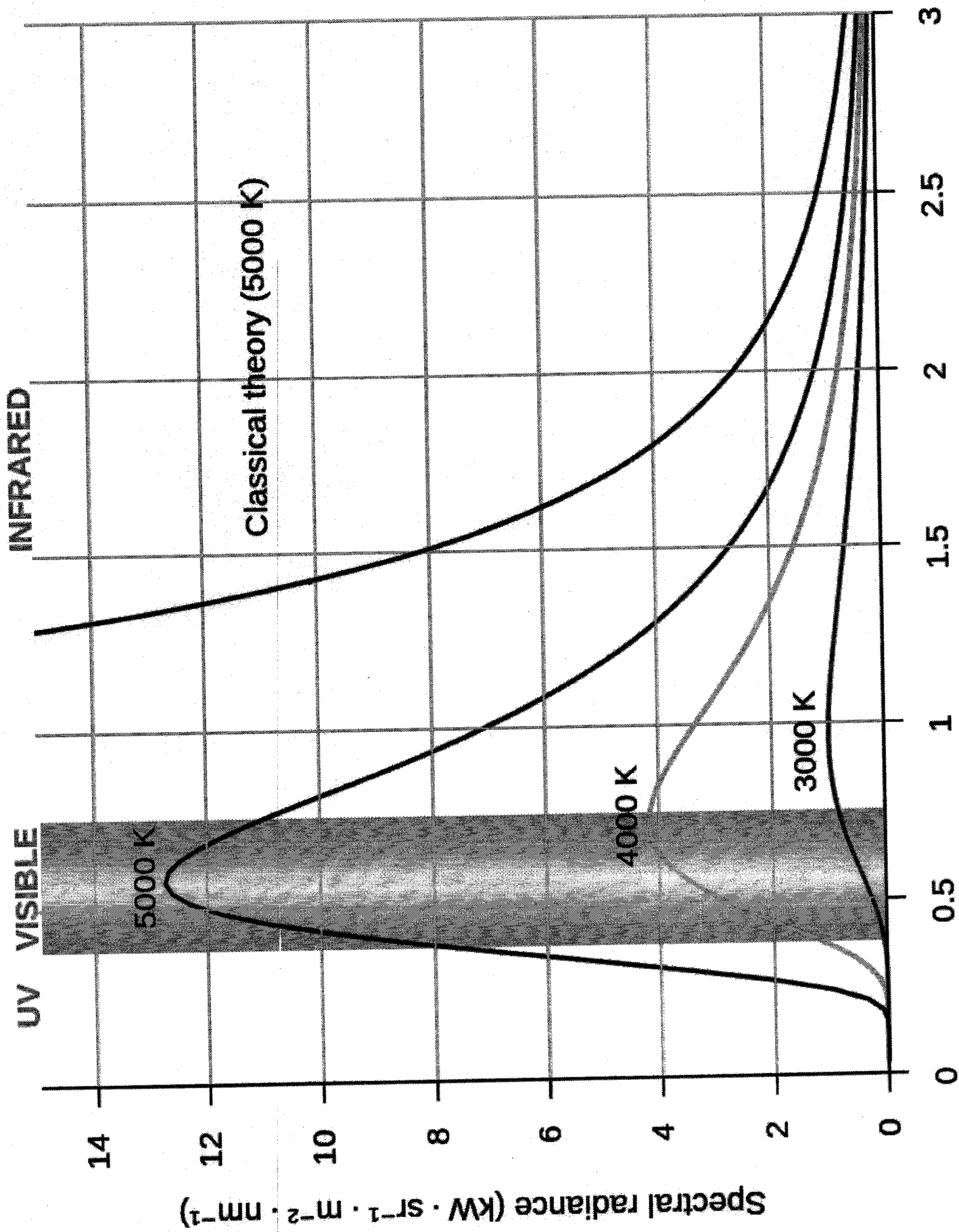
organizing a bit:

$$\rho(\lambda) = \frac{16\pi^2 \hbar c}{\lambda^5} \frac{1}{e^{2\pi \beta \hbar c/\lambda} - 1} \qquad (20)$$

this is plotted in the next page for different temperatures.

Any body at $T \neq 0$ emits radiation over a continuous spectrum. We ($310K$) emit most around the infrared. Light bulbs get hot and start emitting a bit around the visible. The sun is very hot and emits a lot in the visible spectrum.

Source: Wikipedia

(8)

Thermodynamic quantities

Now let us compute the main thermodynamic quantities.

Internal energy

$$U = \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \, \frac{\hbar \omega^3}{e^{\beta \hbar \omega} - 1} \qquad\qquad x = \beta \hbar \omega \qquad dx = \beta \hbar \, d\omega$$

$$= \frac{V}{\pi^2 c^3} \, \hbar \, \frac{1}{(\beta \hbar)^4} \int_0^\infty dx \, \frac{x^3}{e^x - 1}$$

This integral is tabled (you can use Mathematica)

$$\int_0^\infty dx \, \frac{x^3}{e^x - 1} = \frac{\pi^4}{15} \tag{20'}$$

Thus

$$U = \frac{V}{\pi^2 c^3} \, \frac{k_B^4 T^4}{\hbar^3} \, \frac{\pi^4}{15} = \frac{\pi^2 k_B^4}{15 \hbar^3 c^3} \, V T^4$$

For historical reasons, we introduce the Stephan-Boltzmann constant

$$\sigma = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} = 5.67 \times 10^{-8} \, \frac{J}{m^2 s \, K} \tag{21}$$

We then finally get

$$\boxed{U = \frac{4\sigma}{c} V T^4} \tag{22}$$

the total energy in the radiation field scales with T^4, which is a very sharp dependence.

Number of photons in the cavity, Eq (7)

$$N = \sum_{k,\alpha} \frac{1}{e^{\beta\hbar\omega}-1} = \int_0^\infty d\omega \, g(\omega) \frac{1}{e^{\beta\hbar\omega}-1}$$

$$= \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \frac{\omega^2}{e^{\beta\hbar\omega}-1} \qquad\qquad x = \beta\hbar\omega$$

$$= \frac{V}{\pi^2 c^3} \frac{1}{(\beta\hbar)^3} \underbrace{\int_0^\infty dx \frac{x^2}{e^x-1}}_{2.404}$$

$$N = \frac{2.404}{\pi^2 c^3 \hbar^3} k_B^3 \, V T^3 \qquad\qquad (23)$$

Plugging the numbers we get $\qquad\qquad\qquad\qquad (24)$

$$\boxed{N = (2.028 \times 10^7) V T^3}$$

[for V in m^3 and T in K]. Thus, for T = 300 K we find

$$\frac{N}{V} = 5.47 \times 10^{14} \text{ photons}/m^3 \qquad (T=300K)$$

But for T = 6000 K
$$\frac{N}{V} = 4.38 \times 10^{18} \text{ photons}/m^3.$$

The average energy per photon will be

$$\frac{U}{N} = \frac{\dfrac{\pi^2 k_B^4}{15 \hbar^3 c^3} V T^4}{\dfrac{2.404\, k_B^3}{\pi^2 c^3 \hbar^3} V T^3} = \underbrace{\frac{\pi^4}{2.404 \times 15}}_{2.7} k_B T$$

thus

$$\boxed{\frac{U}{N} = 2.7\, k_B T}$$

(25)

Heat capacity

(26)

$$C = \frac{\partial U}{\partial T} = \frac{16\, \sigma V T^3}{c}$$

Free energy, Eq (9)

$$F = k_B T \sum_{\vec{k}, \alpha} \ln(1 - e^{-\beta \hbar \omega_{\vec{k}}}) = k_B T \int_0^\infty d\omega\, g(\omega) \ln(1 - e^{-\beta \hbar \omega})$$

$$= k_B T \frac{V}{\pi^2 c^3} \int_0^\infty d\omega\, \omega^2 \ln(1 - e^{-\beta \hbar \omega}) \qquad x = \beta \hbar \omega$$

$$= k_B T \frac{V}{\pi^2 c^3} \frac{1}{(\beta \hbar)^3} \int_0^\infty dx\, x^2 \ln(1 - e^{-x})$$

$$= \frac{V}{\pi^2 c^3} \frac{k_B^4 T^4}{\hbar^3} \int_0^\infty dx\, x^2 \ln(1 - e^{-x})$$

we may compute this integral by parts

$$\int u \, dv = uv - \int v \, du$$

choose $dv = x^2 dx$, $u = \ln(1 - e^{-x})$. then

$$\int_0^\infty dx \, x^2 \ln(1 - e^{-x}) = \frac{x^3}{3} \ln(1 - e^{-x})\Big|_0^\infty - \int_0^\infty dx \, \frac{x^3}{3} \frac{(+e^{-x})}{1 - e^{-x}}$$

$$\underbrace{\phantom{\frac{x^3}{3}}}_{0}$$

$$= \frac{1}{3} \int_0^\infty dx \, \frac{x^3}{e^x - 1}$$

$$\underbrace{\phantom{\int_0^\infty dx \frac{x^3}{e^x-1}}}_{\pi^4/15 \quad [Eq \ (20')]}$$

Thus

$$F = -\frac{V}{\pi^2 c^3} \frac{k_B^4 T^4}{\hbar^3} \frac{1}{3} \frac{\pi^4}{15}$$

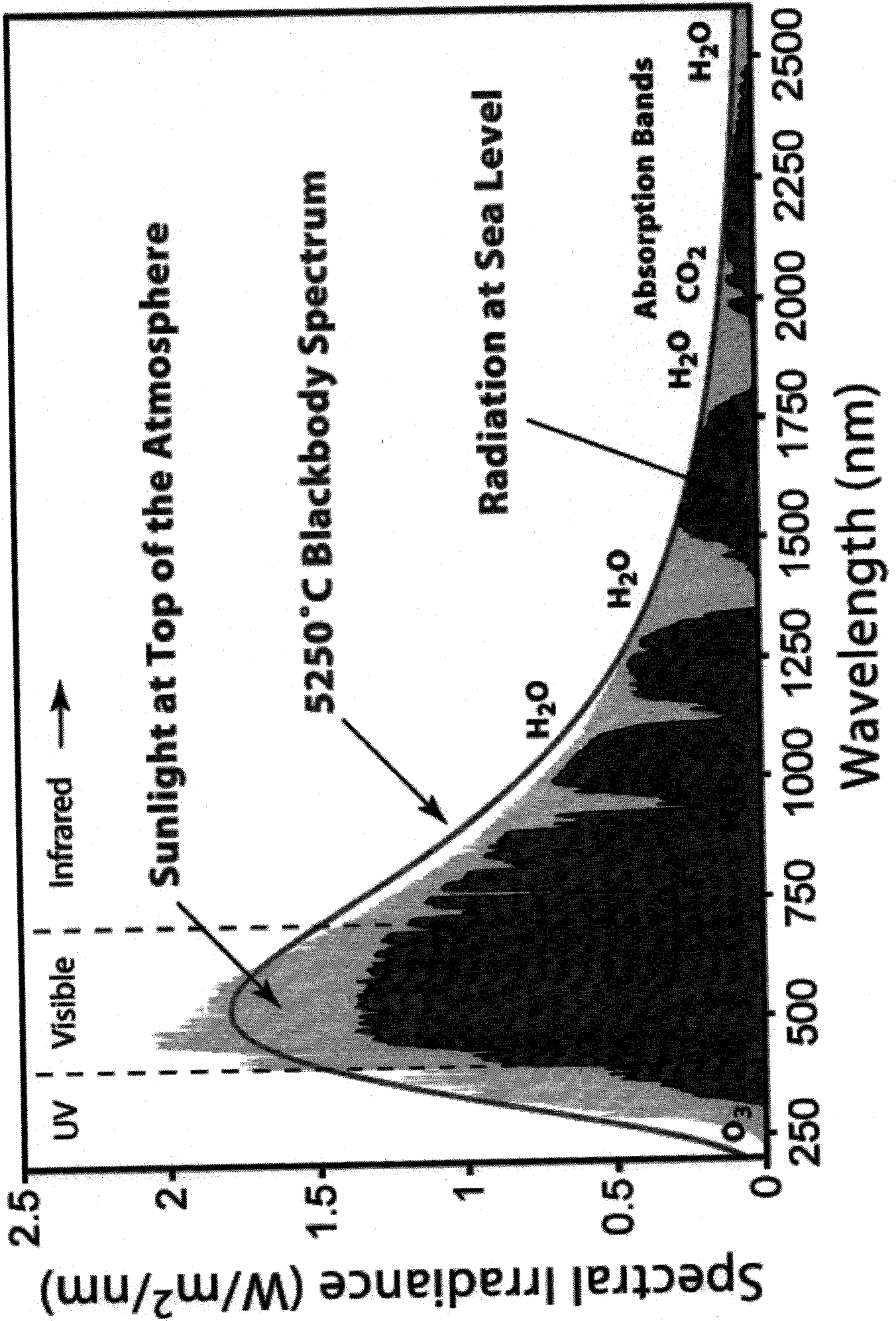$$= -\underbrace{\frac{\pi^2 k_B^4}{45 \hbar^3 c^3}}_{\frac{4\sigma}{3c}} V T^4$$

$$\therefore \boxed{F = -\frac{4\sigma}{3c} V T^4} \qquad (27)$$

Radiation pressure

$$\boxed{P = -\frac{\partial F}{\partial V} = \frac{4\sigma}{3c} T^4 = \frac{U}{3V}} \qquad (28)$$

Solar Radiation Spectrum

UV | Visible | Infrared →

Sunlight at Top of the Atmosphere

5250°C Blackbody Spectrum

Radiation at Sea Level

Absorption Bands
H_2O CO_2 H_2O

H_2O

H_2O

H_2O

O_3

Spectral Irradiance (W/m2/nm)

2.5   2   1.5   1   0.5   0

Wavelength (nm)

250   500   750   1000   1250   1500   1750   2000   2250   2500

(13)

<u>Random topic</u>: <u>equilibrium</u> in <u>the</u> <u>state</u> <u>which</u> <u>minimizes</u>
<u>the</u> <u>free</u> <u>energy</u> $F = U - TS$.

Sorry, I completely forgot to discuss an important interpretation of thermal states. Suppose you have a system with some probabilities P_m. You don't know what they are. they may or may not be equilibrium probabilities.

We can always define the average energy as

$$U = \sum_m E_m P_m \tag{29}$$

and the entropy as

$$\tag{30}$$
$$S = -k_B \sum_m P_m \ln P_m$$

Then we may also define the free energy as

$$\tag{31}$$
$$F = U - TS = \sum_m E_m P_m + k_B T \sum_m P_m \ln P_m$$

this is just a definition. It is true whether or not the P_m are the Gibbs probabilities.

Now comes the cool part: the equilibrium state is exactly that state which minimizes F. So let's prove this: we minimize F by setting

$$\frac{\partial F}{\partial P_m} = 0 \tag{32}$$

we will then show that the P_m which solve these equations are the Gibbs probabilities $e^{-\beta E_m}/z$.

But there is a catch: the P_m must be normalized. this is a constrained minimization problem. To deal with that we introduce a Lagrange multiplier

$$F = \sum_m (E_m + k_B T \ln P_m) P_m + \alpha \left(1 - \sum_m P_m\right) \qquad (33)$$

we then fix α so as to ensure that $\sum_m P_m = 1$.

Now we can compute $\partial F / \partial P_m$:

$$\frac{\partial F}{\partial P_m} = \frac{\partial}{\partial P_m}\left\{ \sum_\ell (E_\ell + k_B T \ln P_\ell) P_\ell + \alpha \left(1 - \sum_\ell P_\ell\right)\right\}$$

$$= \frac{\partial}{\partial P_m}\left[(E_m + k_B T \ln P_m) P_m \right] - \alpha$$

$$= E_m + k_B T \ln P_m + k_B T \frac{P_m}{P_m} - \alpha$$

$$= 0$$

Thus we get

$$k_B T \ln P_m = -E_m + k_B T - \alpha$$

$$\ln P_m = -\beta E_m + 1 - \beta \alpha$$

$$P_m = e^{-\beta E_m} \underbrace{(e^{1 - \beta \alpha})}_{!= \frac{1}{z}}$$

The constant α, or $1/z$, must be set to ensure that $\sum_m P_m = 1$.
It will then be the partition function

(34)

$$\boxed{\begin{array}{c} P_m = \dfrac{e^{-\beta E_m}}{z} \\[2mm] z = \sum_m e^{-\beta E_m} \end{array}}$$

At $T=0$ the system tends to the ground state. So to find the state at $T=0$ we minimize the energy
At $T \neq 0$ we must minimize the free energy $F = U - TS$

Lattice vibrations

Now I want to discuss the vibrations of atoms in a solid. I will show you that, in many aspects, these vibrations are quite similar to electromagnetic radiation.

The potential energy of interaction between two atoms in a solid looks like this
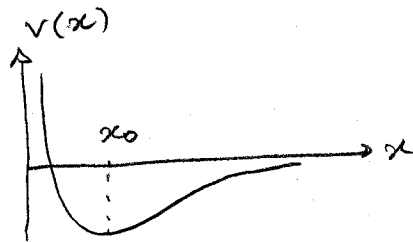
It is usually attractive, except when the atoms get so close that their electronic clouds start repelling each other. This competition creates a minimum at a certain point x_0. This is the equilibrium separation.

But due to thermal fluctuations the atoms will not stand still, but will vibrate around their mean equilibrium positions. Unless we are at high temperatures, these vibrations will generally be small, so we may expand $V(x)$ around their equilibrium positions:
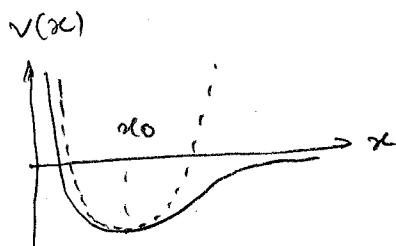
$$V(x) \simeq V(x_0) + \underbrace{V'(x_0)(x-x_0)}_{=0 \text{ because } x_0 \text{ is a minimum}} + \frac{V''(x_0)}{2}(x-x_0)^2 + \dots \qquad (35)$$

$$\quad \text{\small $\llcorner$ } V''(x_0) > 0$$

Let us define $V''(x_0) := g > 0$. This is a constant. It is related to the curvature of the potential at the bottom. We then get

$$V(x) \simeq V(x_0) + \frac{g}{2}(x-x_0)^2 \qquad (36)$$

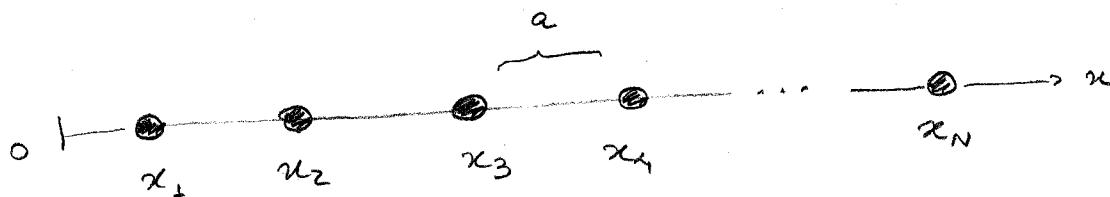This is the <u>harmonic approximation</u>: we approximate the bottom of the potential by a parabola

The harmonic approximation allows us to solve the problem exactly. With the full potential we would only be able to tackle the problem numerically.

— 11 —

The 1D harmonic chain

Now consider the following problem :

we have a "1D crystal" of N atoms. we denote by x_m the equilibrium position of each atom. So if we define the lattice spacing a, then

$$x_m = a m \qquad \begin{cases} x_1 = a \\ x_2 = 2a \\ \vdots \end{cases}$$

the x_m are fixed. they are the positions the atoms would have if they were standing still. we now let X_m be the actual position. we assume that each atom interacts only with its two nearest neighbors. So atom m will interact with $m-1$ and $m+1$. the interaction has the form

$$V(X_m - X_{m+1}) \simeq V(a) + \frac{g}{2} (X_m - X_{m+1} - a)^2$$

It is more convenient to define the relative displacement

$$q_m = X_m - x_m$$

Then we may write

$$V(X_m - X_{m+1}) \simeq V(a) + \frac{g}{2} (q_m - q_{m+1})^2 \qquad (37)$$

the first term is just a constant potential. Energies are always defined up to a constant, so we don't have to worry about it

the total potential energy of the system will then be

$$V = \frac{g}{2}(q_1 - q_2)^2 + \frac{g}{2}(q_2 - q_3)^2 + \ldots + \frac{g}{2}(q_{N-1} - q_N)^2 \qquad (38)$$

But there is one additional twist: we assume periodic boundary conditions. this means we add an additional interaction

$$\frac{g}{2}(q_N - q_1)^2$$

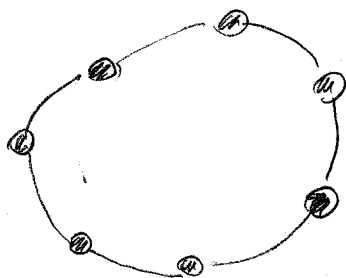You can also interpret this as saying that $q_N = q_0$ or $q_{N+1} = q_1$ or, more generally

$$q_{M+N} = q_M \qquad (39)$$

If you translate by N sites, you get back where you started. Thus, the total potential energy may be written as

$$\boxed{V = \frac{g}{2} \sum_{M=1}^{N} (q_M - q_{M+1})^2} \qquad (40)$$

the sum goes up to N and thus includes the term $(q_N - q_{N+1})^2$, which is $(q_N - q_1)^2$.

Note: periodic BCs is the same as wrapping your 1D chain around to form a ring

Now let's try to construct the classical equations of motion for the system. They read

$$m \, \ddot{q}_m = F_m = - \frac{\partial V}{\partial q_m} \qquad (41)$$

Let's compute this derivative carefully:

$$V = \ldots + \frac{g}{2}(q_{m-2} - q_{m-1})^2 + \frac{g}{2}(q_{m-1} - q_m)^2 + \frac{g}{2}(q_m - q_{m+1})^2$$
$$+ \frac{g}{2}(q_{m+1} - q_{m+2})^2 + \ldots$$

So, when we apply $\partial/\partial q_m$, it will only act on two of these terms:

$$\frac{\partial V}{\partial q_m} = \frac{g}{2}\left\{ \frac{\partial}{\partial q_m}(q_{m-1} - q_m)^2 + \frac{\partial}{\partial q_m}(q_m - q_{m+1})^2 \right\}$$

$$= \frac{g}{2}\left\{ 2(q_{m-1} - q_m)(-1) + 2(q_m - q_{m+1})(1) \right\}$$

$$= g(q_{m-1} - 2q_m + q_{m+1})$$

Thus the equations of motion will be

$$m \, \ddot{q}_m = g(q_{m-1} - 2q_m + q_{m+1}) \qquad (42)$$

These are couple equations. If $N \sim 10^{23}$ then we would have to simultaneously solve all 10^{23} equations. So at first, this seems like a hard problem. It is a remarkable fact that these equations can actually be solved exactly. This is a consequence of the harmonic approximation. If we had not used it, we would be in real trouble.

Before we try to solve Eq (42) let us derive it in a fancier way. We may define a Lagrangian for our system

$$\mathcal{L} = \sum_{m=1}^{N} \frac{m}{2} \dot{q}_m^2 \ - \ \frac{g}{2} \sum_{m=1}^{N} (q_m - q_{m+1})^2 \tag{43}$$

we now apply the Euler - Lagrange equations

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{q}_m} \right) - \frac{\partial \mathcal{L}}{\partial q_m} = 0 \tag{44}$$

we have

$$\frac{\partial \mathcal{L}}{\partial \dot{q}_m} = m \dot{q}_m \quad \leadsto \quad \frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{q}_m} \right) = m \ddot{q}_m$$

$$\frac{\partial \mathcal{L}}{\partial q_m} = - \frac{\partial V}{\partial q_m} = - g(q_{m-1} - 2q_m + q_{m+1})$$

Thus we again get (42)

Solution of the Eqs of motion

Whenever you see linear equations of motion, you can always solve them by the following trick: try the ansatz

$$q_m(t) = A_m e^{-i\omega t} \tag{45}$$

where A_m and ω are constants to be determined. Substituting in (42) then gives

$$m\ddot{q}_m = m A_m (-i\omega)^2 e^{-i\omega t} = -m A_m \omega^2 e^{-i\omega t}$$

and

$$g(q_{m-1} - 2q_m + q_{m+1}) = g(A_{m-1} e^{-i\omega t} - 2A_m e^{-i\omega t} + A_{m+1} e^{-i\omega t})$$

The factor of $e^{-i\omega t}$ appears everywhere so we may cancel it out. We then get

$$\boxed{- m\omega^2 A_m = g(A_{m-1} - 2A_m + A_{m+1})} \tag{46}$$

This is an _algebraic equation_. This is the magic of _linearity_ (ie of the harmonic approximation): it leads to algebraic, instead of differential equations

$$\boxed{\text{Harm. approx.} \rightsquigarrow \text{linear ODEs} \xrightarrow{e^{-i\omega t}} \text{linear algebraic equations}} \tag{47}$$

Let us write (46) as

$$\frac{g}{m}(-A_{m-1} + 2A_m - A_{m+1}) = \omega^2 A_m \tag{48}$$

we now group the A_m into a vector

$$\vec{A} = \begin{pmatrix} A_1 \\ A_2 \\ \vdots \end{pmatrix} \tag{49}$$

then we define a matrix, for instance if $N=5$

$$\left(\begin{matrix}\text{Example} \\ \text{with } N=5\end{matrix}\right) \qquad W = \frac{g}{m} \begin{pmatrix} 2 & -1 & 0 & 0 & -1 \\ -1 & 2 & -1 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 \\ 0 & 0 & -1 & 2 & -1 \\ -1 & 0 & 0 & -1 & 2 \end{pmatrix} \tag{50}$$

Notice the solitary (-1)'s in the corners: they come from the periodic boundary conditions.

We may now write (48) as

$$\boxed{W\vec{A} = \omega^2 \vec{A}} \tag{51}$$

this is an eigenvalue/eigenvector eq. We started with (45), which had as unknowns ω and A_m. We now see that ω^2 is simply the eigenvalue of W and A_m are the eigenvectors. We have reduced the solution of Newton's equations to a linear algebra problem.

At first you may think: well, let's plug W into Mathematica and ask it to find all eigenvalues and eigenvectors. Unfortunately there is a problem: we are talking about a crystal here so N will be enormous. The computational approach is often used for molecules (even big ones like DNA). But for crystal we need another method.

The matrix W in Eq (50) has a very special structure. It is called a cyclic matrix: take each line and rotate the entries around to the right; you will get the line below

$$
\begin{array}{ccccc}
\overset{\frown}{2} & -1 & 0 & 0 & -1 \\
-1 & 2 & -1 & 0 & 0
\end{array}
$$

Cyclic matrices can always be diagonalized by a discrete Fourier transform.

To do that we start at (48) and we try the ansatz

$$
A_m = B \, e^{i k x_m} \quad , \quad x_m = am \tag{52}
$$

the introduction of x_m here is just for convenience; it makes k have units of wave-vector. We will soon see that it looks something like momentum. Here B and k are constants to be determined.

Substituting (52) into (48) then gives

$$A_{m+1} = B\, e^{ikx_{m+1}} = B\, e^{ik(m+1)a}$$

$$= B e^{ikx_m} e^{ika}$$

$$A_{m-1} = B e^{ikx_m} e^{-ika}$$

Thus (48) becomes

$$\frac{g}{m}\left(-e^{-ika} + 2 - e^{ika}\right) B e^{ikx_m} = \omega^2 B e^{ikx_m}$$

cancelling out the term $B e^{ikx_m}$ we then get

$$\omega^2 = \frac{g}{m}\left(2 - e^{ika} - e^{-ika}\right)$$

$$= \frac{g}{m}\left(2 - 2\cos ka\right)$$

Thus we conclude that the ansatz (52) indeed works, producing

a frequency

$$\boxed{\omega_k = \sqrt{\frac{2g}{m}\left(1 - \cos ka\right)}}$$ (53)

this is a <u>dispersion</u> <u>relation</u>; it relates frequency ω with wave-vector k.

We still haven't used the periodic boundary conditions. It will determine the allowed values of k. We have

$$A_{m+N} = B e^{i k x_m} e^{i k a N} = B e^{i k x_m} = A_m$$

Thus

$$e^{i k a N} = 1$$

this implies that

$$k a N = 2\pi \ell, \qquad \ell = 0, \pm 1, \pm 2, \cdots$$

or

$$\boxed{k = \frac{2\pi \ell}{N a}, \quad \ell = 0, \pm 1, \pm 2, \cdots}$$

Compare this to Eq (14): they are absolutely identical because $Na = L$ is the length of the chain. I told you: momentum is always quantized in this way.

But in the present problem there is an additional property: each value of k will define a different eigenvector: $A_m = B e^{i k m}$ so

$$\vec{A} \qquad B \begin{pmatrix} e^{i k a} \\ e^{2 i k a} \\ \vdots \end{pmatrix}$$

k is actually the label of the eigenvalues / eigenvectors. But our matrix W is $N \times N$ and must therefore have N eigenvectors, whereas Eq (54) actually gives an infinite number of k values

The resolution of this paradox lies in the fact that, if you translate k by $2\pi/a$ you get the same state

$$e^{i(k+2\pi/a)x_m} = e^{ikx_m} \underbrace{e^{i(\frac{2\pi}{a})ma}}_{e^{2\pi im} = 1}$$

So we only need to take eigenvectors with k within an interval of length $2\pi/a$. The actual interval is arbitrary, but the most popular choice is

$$k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right] \qquad (55)$$

In condensed matter we call this the first Brillouin zone. We therefore take

$$\boxed{k = \frac{2\pi \ell}{Na}, \qquad \ell = -\frac{N}{2}, -\frac{N}{2}+1, \dots, \frac{N}{2}-1, \frac{N}{2}} \qquad (56)$$

ℓ takes on N distinct values in the interval $-\frac{N}{2} < \ell \le \frac{N}{2}$. This gives us the N distinct eigenvectors $\vec{A}_k$, with components

$$A_{k,m} = B e^{ikx_m}.$$

But what about B? Well, it must follow from the normalization condition of the eigenvectors

$$1 = \sum_{m=1}^{N} |A_{k,m}|^2 = \sum_{m=1}^{N} |B|^2 = N|B|^2$$

The customary choice is to take B real, which implies $B = 1/N$. Thus we finally conclude that

$$
\text{Eigenvectors of the cyclic matrix } w \text{ in (50)}
$$

$$
\vec{A_k} = \frac{1}{\sqrt{N}} \begin{pmatrix} e^{ika} \\ e^{2ika} \\ \vdots \end{pmatrix} \qquad A_{k,m} = \frac{1}{\sqrt{N}} e^{ikx_m}
$$

$$
k = \frac{2\pi\ell}{Na} \qquad \frac{-N}{2} < \ell \leq \frac{N}{2}
$$

$$
k \in \left[-\frac{\pi}{a}, \frac{\pi}{a} \right]
$$

(57)

This is a very important result. It is true for a matrix of arbitrary size, as long as it is cyclic. And cyclic matrices appear quite often in all areas of physics.

If we now return to Newton's law (42), we see that **one** possible solution will be

$$
q_m(t) = e^{i(kx_m - \omega_k t)}
$$

(56)

This is a __plane wave__: vibrations propagate through matter like waves. The most general solution will then be given by linear combinations of plane waves

$$
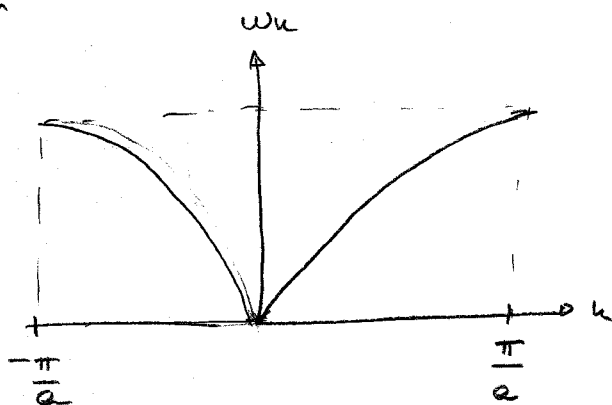\left(\begin{array}{c} \text{General} \\ \text{Solution} \end{array} \right) \qquad q_m(t) = \sum_k c_k\, e^{i(kx_m - \omega_k t)}
$$

(57)

where the c_k are coefficients determined by the initial conditions

Now let's reexamine the eigenvalues ω_k:

$$\omega_k = \sqrt{\frac{2g}{m}(1 - \cos ka)} \qquad (58)$$

This is the dispersion relation for vibrational waves. It looks like this

At long wavelengths $(ka \ll 1)$ we may expand
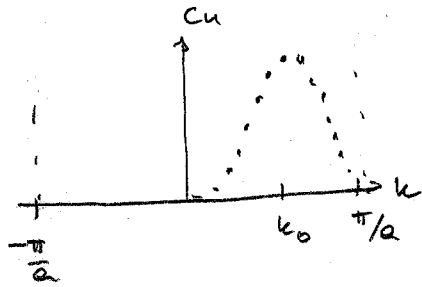
$$\cos ka \simeq 1 - \frac{(ka)^2}{2}$$

which gives

$$\omega_k \simeq \sqrt{\frac{2g}{m} \frac{k^2 a^2}{2}}$$

or

$$\boxed{\omega_k \simeq c|k| \qquad c = \sqrt{\frac{g a^2}{m}}} \qquad (59)$$

This looks just like the electromagnetic dispersion relation. But now c is not the speed of light. It is the _speed of sound_.

The general wave evolves in time as in Eq (57). Suppose that the coefficients c_k are peaked around a certain value k_0

Then we may expand

$$\omega_k \simeq \omega_{k_0} + \omega'_{k_0} (k - k_0)$$

Then

$$k x_m - \omega_k t = (k - k_0) x_m + k_0 x_m - \omega_{k_0} t - \omega'_{k_0} (k-k_0) t$$

$$= (k - k_0)(x_m - \omega'_{k_0} t) + k_0 x_m - \omega_{k_0} t$$

Eq (57) then becomes

$$q_m(t) \simeq e^{i(k_0 x_m - \omega_{k_0} t)} \sum_k c_k e^{i(k - k_0)(x_m - \omega'_{k_0} t)} \tag{60}$$

The first term is just a phase factor. It describes the propagation of a perfect plane wave with frequency ω_{k_0}, moving with <u>phase velocity</u>

$$\text{phase velocity} = \frac{\omega_{k_0}}{k_0}$$

The remaining term in (60) gives the motion of the wave packet as a whole, which occurs with group velocity v_k, or

$$\boxed{\text{group velocity}: \quad v_k = \frac{\partial \omega_k}{\partial k}}$$

(61)

For our dispersion relation it is convenient to work

$$1 - \cos ka = 2 \sin^2 \left(\frac{ka}{2} \right)$$

Then we get

$$\omega_k = \sqrt{\frac{4g}{m}} \left| \sin \left(\frac{ka}{2} \right) \right|$$

(62)

then

$$\frac{\partial \omega_k}{\partial k} = \sqrt{\frac{4g}{m}} \frac{a}{2} \cos \left(\frac{ka}{2} \right)$$

the group velocity will then be

$$v_k = c \cos \left(\frac{ka}{2} \right)$$

(63)

this shows that the speed of sound actually depends on the k value. When $ka \ll 1$ then $v_k \simeq c$. But in the other extreme case, when $k \simeq \pm \pi/a$ then $v_k = 0$. Vibrations with really high momentum generate stationary waves (zero group velocity).

We can see this by looking at the eigenvectors

$$A_{k m} = \frac{1}{\sqrt{N}} e^{i k m a}$$

If $k = \pi/a$ this gives

$$A_{\pi/a, m} = \frac{1}{\sqrt{N}} e^{i \pi m} = \frac{1}{\sqrt{N}} (-1)^M$$

Thus, the vibration with $k = \pi/a$ (boundary of the Brillouin zone) is a vibration where each atom is completely out-of-phase with its neighbors

$(-1)^M$:

This is a stationary wave so it has $v_u = 0$.

Phonons

The most general solution to our problem in Eq (57)

$$q_m(t) = \sum_k c_k e^{i(k x_m - w_k t)}$$

Let us define a new set of variables

$$Q_k = c_k e^{-i w_k t} \qquad (64)$$

Then

$$q_m = \sum_k Q_k e^{i k x_m} \qquad (65)$$

The variables Q_k and q_m are Fourier transforms of each other. The variable Q_k satisfies the differential equation

$$\ddot{Q}_k = -w_k^2 Q_k \qquad (66)$$

which is the equation of a harmonic oscillator with frequency w_k.

What we have just done is known as the <u>normal mode</u> <u>decomposition</u>. We started with a problem of N variables q_m which interact with each other [Eq (46)]. Then we made a transformation to a new set of coordinates Q_k [Eq (65)] in such a way that these new variables are completely independent of each other. The Q_k are the <u>normal modes</u> of the system.

It is now straightforward to quantize our theory. Each Q_k behaves like a harmonic oscillator and will therefore have energies

$$\hbar \omega_k (n_k + 1/2) \qquad n_k = 0, 1, 2, 3, \dots$$

[Please do not confuse n_k with $n k$].

The total energy of the system will be

$$E = \sum_k \hbar \omega_k (n_k + 1/2) \qquad (67)$$

When we quantize the theory we discover that vibrations themselves are quantized. If $n_{k_0} = 3$ for some k_0 we say our system has "3 $\underline{quanta}$ $\underline{of}$ $\underline{vibration}$ $\underline{with}$ $\underline{momentum}$ k_0".

These quanta of vibration behave exactly like particles, analogously to photons. They are called phonons.

$$\boxed{\text{Phonon} = \text{quanta of vibration}} \qquad (68)$$

They are not actual particles. But for every intents and purposes, they behave like particles. We call them $\underline{quasi\text{-}particles}$.

This is how we do things in condensed matter nowadays. We describe all processes occurring at the microscopic level in terms of quasi-particles (which we also call "$\underline{excitations}$").

All processes occurring in a solid may then be related to these quasi-particles and how they interact, among each other and with actual particles such as electrons.

	Name	Field
→	Electron	—
∿	Photon	Electromagnetic wave
∿	Phonon	Elastic wave
⊣⊢	Plasmon	Collective electron wave
⧢	Magnon	Magnetization wave
–	Polaron	Electron + elastic deformation
–	Exciton	Polarization wave

Figure 1 Important elementary excitations in solids.

Classical field theories

Let's go back to the start

$$m \ddot{q}_m = g(q_{m-1} - 2q_m + q_{m+1}) \tag{69}$$

Now we assume that the lattice spacing is very small so we don't have to worry about the fine details about the individual sites. So we think about taking a <u>continuum limit</u>. Each q_m represents the displacement at position x_m, so we define a continuous <u>displacement field</u>

$$\phi(x_m) = \frac{q_m}{\sqrt{a}} \tag{70}$$

I know this seems weird, but it will make sense in a moment. The LHS of (69) then becomes

$$m \ddot{q}_m = \sqrt{a} \, m \left(\frac{\partial^2 \phi}{\partial t^2} \right)$$

As for the RHS, we see the appearance of a 2nd derivative

$$q_{m-1} - 2q_m + q_{m+1} = \sqrt{a} \left[\phi(x_{m-1}) - 2\phi(x_m) + \phi(x_{m+1}) \right]$$

$$\approx \sqrt{a} \; a^2 \frac{\partial^2 \phi}{\partial x^2}$$

We then get

$$m\sqrt{a}\ \frac{\partial^2 \phi}{\partial t^2} = g\sqrt{a}\ a^2\ \frac{\partial^2 \phi}{\partial x^2}$$

we see here the appearance of the speed of sound (59),

$$c^2 = \frac{g a^2}{m}$$

we then get a <u>wave equation</u>

$$\boxed{\frac{\partial^2 \phi}{\partial t^2} = c^2\ \frac{\partial^2 \phi}{\partial x^2}}$$

(71)

In the continuum limit the discrete q_n are replaced by a continuous field $\phi(x,t)$, which satisfies a wave equation. This in the <u>theory of elasticity</u>: we describe deformations in a body by a continuous field $\phi(x,t)$ describing the displacement at position x and time t.

If we plug in a plane-wave solution $e^{i(kx - \omega t)}$ in Eq (71) we will find that it is a solution only if $\omega = c|k|$. Thus, we conclude that when we take the continuum limit we wash away the high k physics and keep only the <u>long wavelength</u> (<u>low energy</u>) <u>phenomena</u>.

The phonon picture can also be made to appear here. Now phonons are the elementary excitations of the displacement field, just like photons are the excitations of the electromagnetic fields and electrons are the excitations of the Dirac field. This is <u>quantum field theory</u>. It unifies all areas of physics by interpreting elementary particles and quasi-particles as the elementary excitations of quantum fields.

Figure 22.14
Typical dispersion curves along a general direction in k-space for a lattice with a two-ion basis. The three lower curves (acoustic branches) are linear in k for small k. The three upper curves (optical branches) will be quite flat if the intracellular interactions are much stronger than those between cells. Note that the direction of k is not one of high symmetry, since there is no degeneracy.

$\omega(k)$

k

Optical branches little to the specific heat contribute
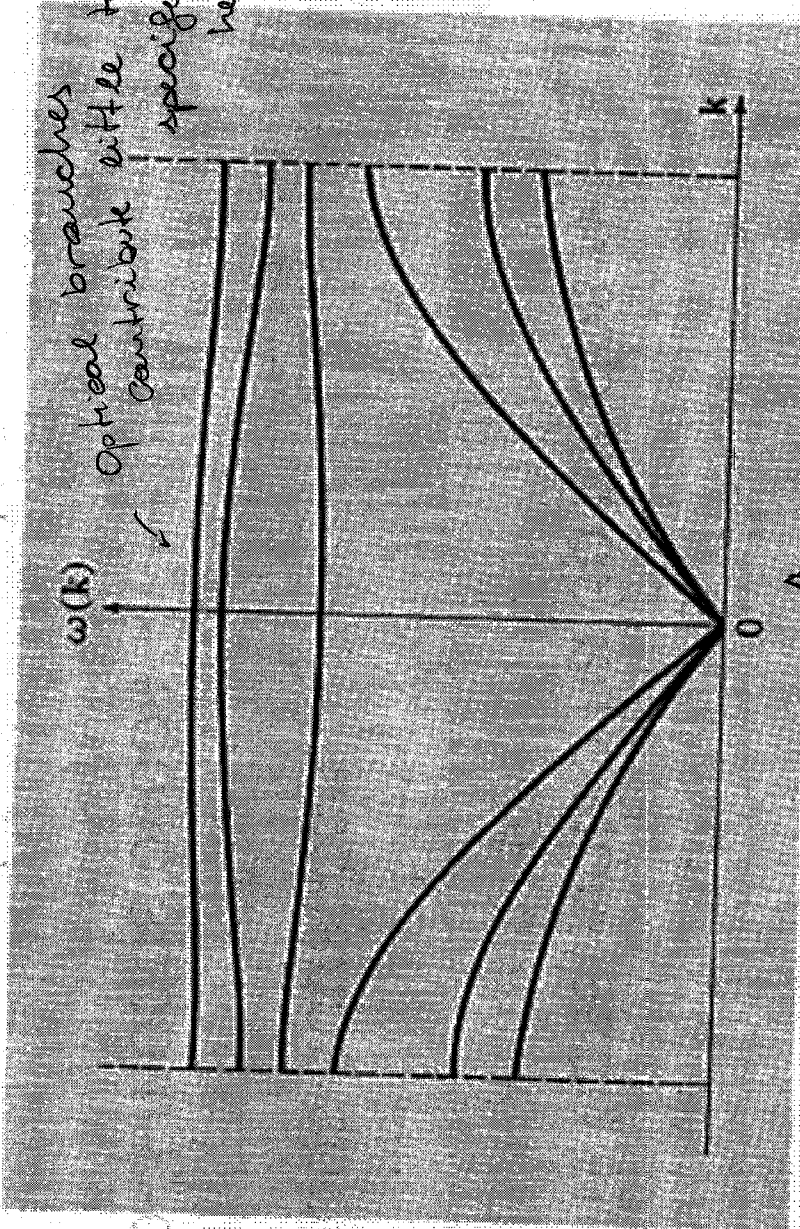
there are always 3 acoustic branches

$\omega_k = c |k|$

Lecture 3D

Normal Modes of a Monatomic Three-Dimensional Bravais Lattice
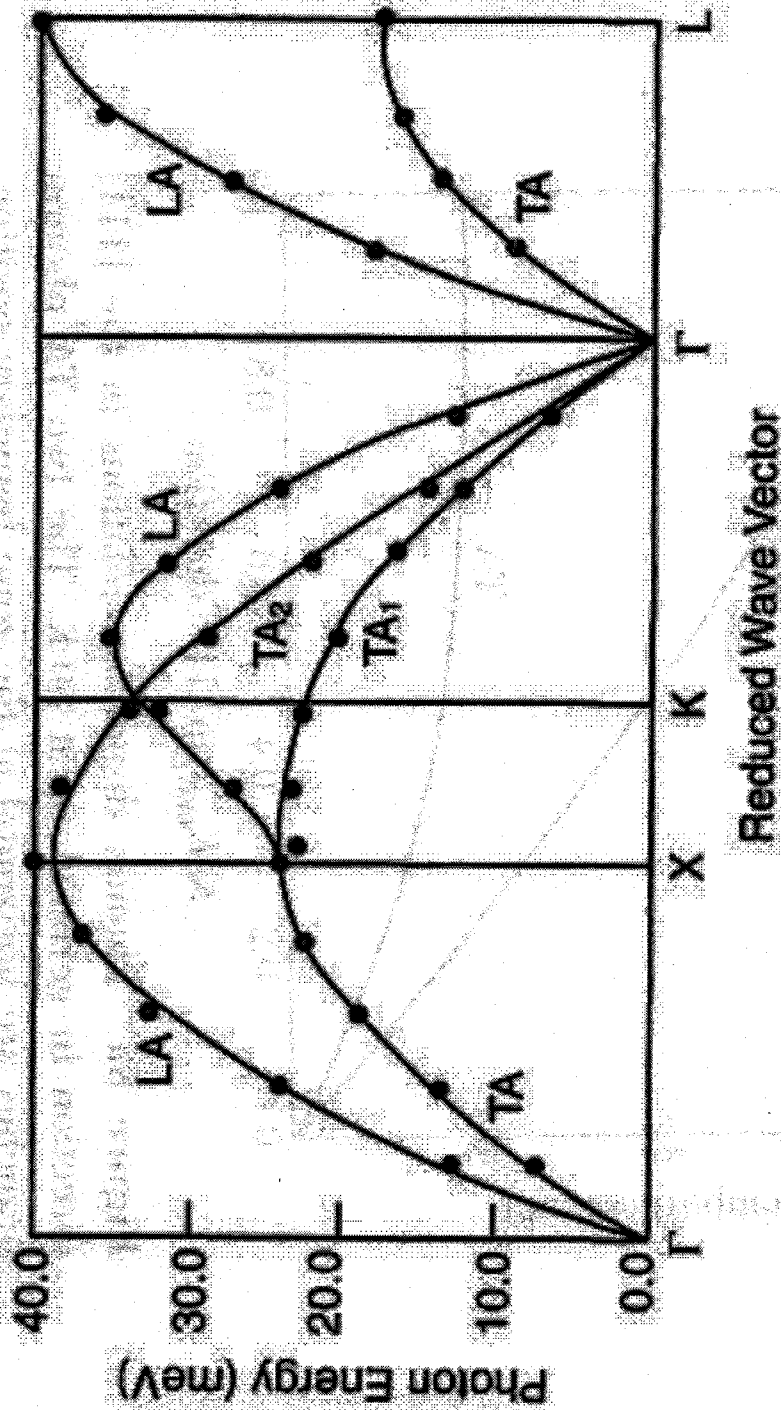

(a)

SOLID STATE PHYSICS
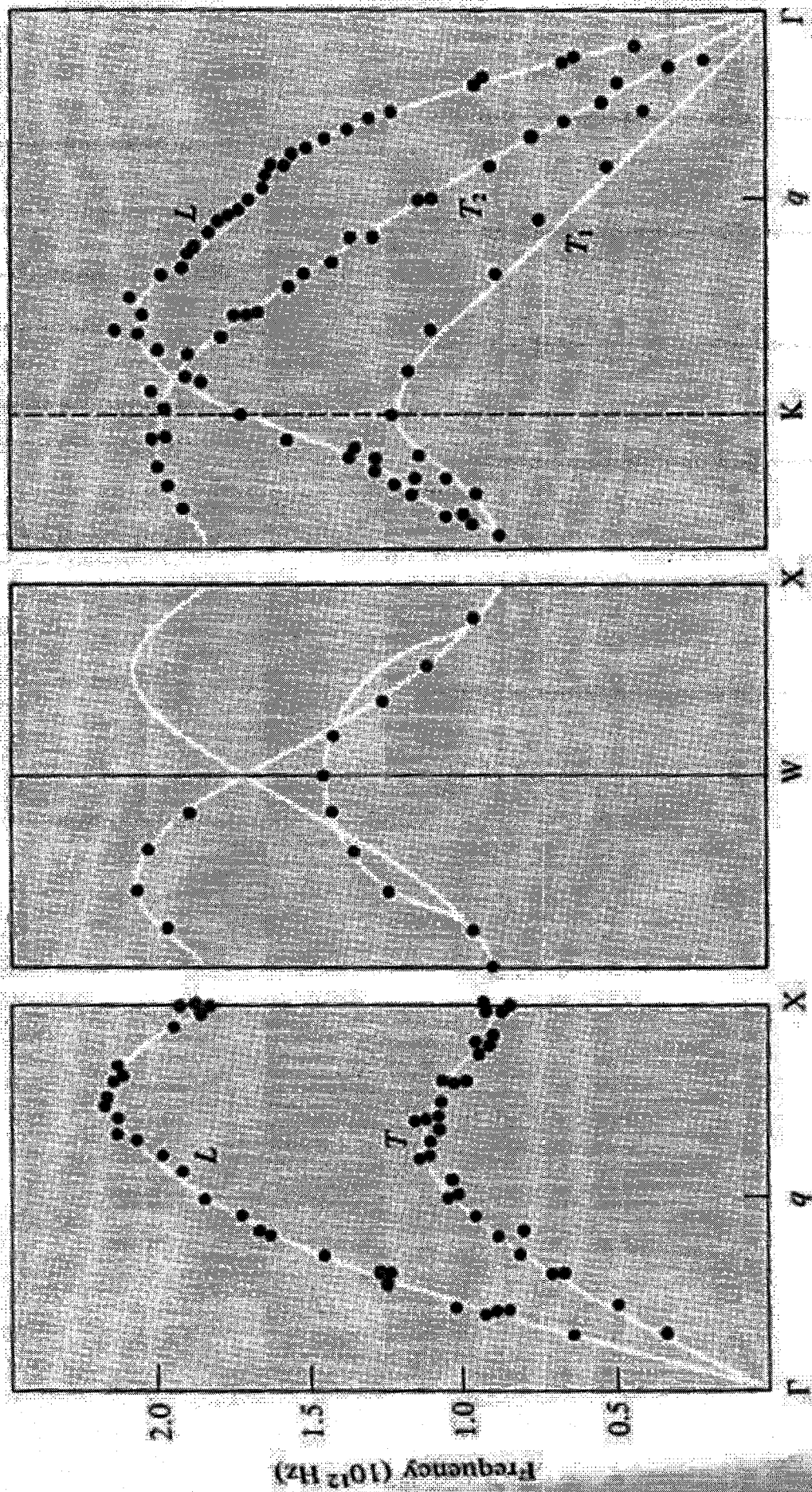
Fig. 5 Phonon dispersion curves of aluminum along symmetry directions. The solid lines represents the calculations of A. A. Quong and B. M. Klein, Phys. Rev. B46, 10734 (1992) (copyright 1992 by the American Physical Society). Longitudinal and transverse acoustic branches are indicated by LA and TA (or TA_1 and TA_2), respectively. The experimental points are from the papers of G. Gilat and R. M. Nicklow, Phys. Rev. 143, 487 (1966) and R. Stedman, S. Almqvist and G. Nilsson, Phys. Rev. 162, 549 (1967).
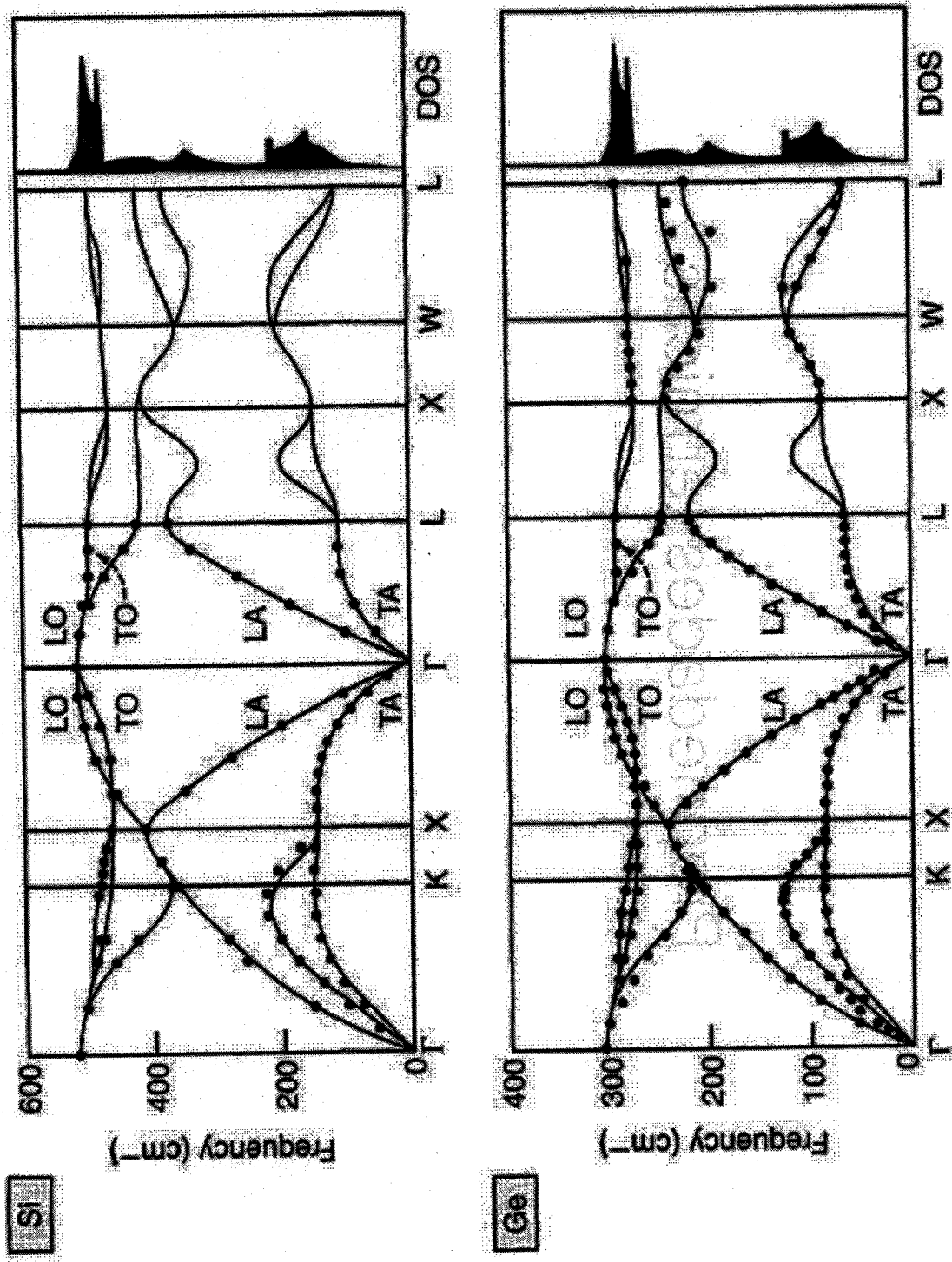
Fig. 6 Phonon dispersion curves and density-of-states of Si and Ge calculated by P. Giannozzi, S. de Gironcoli, P. Pavone and S. Baroni, Phys. Rev. B43, 7231 (1991) (copyright 1991 by the American Physical Society). Longitudinal and transverse acoustic (or optical) modes are indicated by LA and TA (LO and TO), respectively. The experimental points are from G. Dolling, in "Inelastic Scattering of Neutrons in Solids and Liquids" edited by S. Ekland (IAEA, Vienna 1963) Vol.II, p.37; G. Nilsson and G. Nelin, Phys. Rev. B3, 364 (1971) and Phys. Rev. B6, 3777 (1972). Conversion to meV units can be done noting that 1 cm$^{-1} =$ 0.124 meV.

If you multiply a vector $\vec{c}$ by F_N you take the discrete
Fourier transform of this vector

$$\vec{c} = F_N \, \vec{y}$$

(79)

$$c_\ell = \sum_m e^{2\pi i \ell m / N} y_m$$

the Fourier matrix is unitary

$$F F^\dagger = F^\dagger F = N I \,, \quad I = \text{identity matrix} \qquad (80)$$

The Fourier transform takes functions in real space
$y(x)$ to functions in frequency space $c(k)$, and
vice-versa. In the computer you do that by multiplying
by F_N: if $\vec{y}$ is a data-set in real space, then $F_N \vec{y} = \vec{c}$
is the frequency space representation of that data-set.

In general to compute $F_N \vec{y}$ you need N^2 multiplica-
tions. Around 1965 J. Cooley and J. Tukey showed that
you can actually do this with only $N \ln N$. That is a huge
improvement. this is the FFT algorithm.

Now let

$$\boxed{\omega = e^{2\pi i/N}} \tag{72}$$

we then get

$$\vec{A}_\ell = \frac{1}{\sqrt{N}} \begin{bmatrix} \omega^\ell \\ \omega^{2\ell} \\ \omega^{3\ell} \\ \vdots \\ \omega^{N\ell} \end{bmatrix} \tag{73}$$

If we choose to label the m also as

$$m = 0, 1, \ldots, N-1$$

then

$$A_{\ell m} = \frac{1}{\sqrt{N}} \omega^{\ell m} \tag{74}$$

the matrix whose columns are the eigenvectors $\vec{A}_\ell$ is called the Fourier matrix (we forget about the $1/\sqrt{N}$)

$$F_N = \begin{bmatrix} 1 & 1 & 1 & 1 & \cdots \\ 1 & \omega & \omega^2 & \omega^3 & \cdots \\ 1 & \omega^2 & \omega^4 & \omega^6 & \cdots \\ \vdots & \vdots & \vdots & & \ddots \\ 1 & \omega^N & \omega^{2N} & \omega^{3N} & \end{bmatrix} \tag{75}$$

or

$$\boxed{(F_N)_{\ell m} = \omega^{\ell m}, \qquad \omega = e^{2\pi i/N} \\ \ell, m = 0, \ldots, N-1} \tag{78}$$

The Fast Fourier Transform

Around Eq (50) we discussed the diagonalization of a cyclic matrix

$$W = \frac{g}{m} \begin{bmatrix} 2 & -1 & 0 & 0 & -1 \\ -1 & 2 & -1 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 \\ 0 & 0 & -1 & 2 & -1 \\ -1 & 0 & 0 & -1 & 2 \end{bmatrix} \qquad (68)$$

We found that the eigenvectors have the form

$$\vec{A}_k = \frac{1}{\sqrt{N}} \begin{bmatrix} e^{ika} \\ e^{2ika} \\ \vdots \\ e^{ikNa} \end{bmatrix} \qquad k = \frac{2\pi \ell}{Na} \qquad (69)$$

Before we were using $k \in [-\frac{\pi}{a}, \frac{\pi}{a}]$. Now let's choose $k \in [0, 2\pi/a]$. To do that we choose

$$\ell = 0, 1, \ldots, N-1 \qquad (70)$$

then

$$k\, x_m = \frac{2\pi \ell}{Na}\, ma = \frac{2\pi\, m \ell}{N} \qquad (71)$$

The eigenvectors then became

$$\vec{A}_\ell = \frac{1}{\sqrt{N}} \begin{bmatrix} e^{i2\pi \ell/N} \\ e^{i2\pi 2\ell/N} \\ \vdots \\ e^{i2\pi N\ell/N} \end{bmatrix}$$

the key idea of the FFT algorithm is to relate F_N with $F_{N/2}$. So if we assume that $N = 2^L$, we may _recursively_ _chop down_ F_{24} in terms of smaller and smaller matrices. To do that we divide $y_0, y_1, \cdots, y_{N-1}$ into even and odd components. Let $M = N/2$. then

$$c_\ell = \sum_{m=1}^{N-1} \omega_N^{\ell m} y_m$$

$$= \sum_{m=0}^{M-1} \omega_N^{\ell 2m} y_{2m} + \sum_{m=0}^{M-1} \omega_N^{\ell(2m+1)} y_{2m+1}$$

But

$$\omega_N = e^{2\pi i / N} \implies \omega_N^2 = e^{4\pi i / N} = \omega_M$$

thus

$$c_\ell = \sum_{m=0}^{M-1} \omega_M^{\ell m} y_{2m} + \omega_N^\ell \sum_{m=0}^{M-1} \omega_M^{\ell m} y_{2m+1}$$

the two sums are now $F_{N/2}$ acting on smaller vectors.

(44)

we can write this as the matrix decomposition

$$
F_N = \begin{bmatrix} I_{N/2} & D_{N/2} \\ I_{N/2} & -D_{N/2} \end{bmatrix} \begin{bmatrix} F_{N/2} & 0 \\ 0 & F_{N/2} \end{bmatrix} \begin{bmatrix} 0,2,4,6\cdots \\ 1,3,5,7,\cdots \end{bmatrix}
$$

where $I_{N/2}$ is the identity matrix and

$$
D_M = \operatorname{diag}(1, \omega_N, \omega_M^2, \ldots, \omega_M^{M-1})
$$

Then we decompose the inner matrix again

$$
\begin{bmatrix} F_{N/2} & 0 \\ 0 & F_{N/2} \end{bmatrix} = \begin{bmatrix} I_{N/4} & D_{N/4} & 0 & 0 \\ I_{N/4} & -D_{N/4} & 0 & 0 \\ 0 & 0 & I_{N/2} & D_{N/2} \\ 0 & 0 & I_{N/2} & -D_{N/2} \end{bmatrix} \begin{bmatrix} F_{N/4} & & & \\ & F_{N/4} & & \\ & & F_{N/4} & \\ & & & F_{N/4} \end{bmatrix} \times
$$

$$
\times \begin{bmatrix} 0,4,8,\cdots \\ 2,6,10,\cdots \\ 1,5,9,\cdots \\ 3,7,11,\cdots \end{bmatrix}
$$

If $N = 2^L$ this will require, in total $\frac{NL}{2}$ matrix multiplications, instead of N^2.

Ex: $N = 1024 = 2^{10} \Rightarrow L = 10$.

$$
(1024)^2 \approx 1 \text{ million}
$$
$$
1024 \times \frac{10}{2} \approx 5000
$$

$\Big\}$ 200 times faster