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If a steel rod is hung by a thread and struck at the lower
end, an audible metallic "ring" is produced whose fundamental fre-
quency depends on the velocity of sound in steel and on the length
of the rod. At the very point of impact on the rod, a compressional
wave is started which emenates outward and returns from free surfaces
as rarefaction waves. Most of the waves cancel out except those
whose wavelength are multiples of the rod dimensions. The initial
energy imparted to the rod is ultimately dissipated as heat but only
after a relatively long period of time. A small amount of the energy
is transferred to the air as a sound w... (this is the portion we
hear). The waves we have induced in the rod are actually identical
to the very long wavelength phonons (or normal modes) already present
in the rod as part of the normal thermal spectrum of phonons. When
the rod is struck, this portion of the phonon spectrum is considerably
enhanced, but only after many seconds does this energy redistribute
itself so that thermal equilibrium is re-established. On the other
hand if an X-ray beam strikes the rod, it will produce phonons whose
frequency is $\sim 10^{12}$–10^{13} hertz, at least 10^9 times greater than the
audible frequencies created by mechanical striking. Furthermore,
rather than taking seconds to reach thermal equilibrium, the time
required is only $\sim 10^{-12}$ seconds for these high frequency phonons.
The reason for this difference in behavior between the low frequency
phonons and the high frequency phonons is well understood in terms
of anharmonicity.

The electrons binding atoms together in a solid can (in
a crude first approximation) be considered to be replaced by springs
joining nearest and next nearest neighbors. For small atomic displace-

ments the forces created by these springs are harmonic (quadratic potential energy). Within this approximation, the atoms and springs become a system of coupled harmonic oscillators and this gives rise to the normal modes (or phonons) which are excited according to the usual exponential Boltzman partition function depending on the temperature of the system and the frequency of the phonon. However, in reality, a system in which the forces between atoms are truly harmonic can never reach thermal equilibrium since the phonons have no means for exchanging energy with each other. The introduction of anharmonicity, i.e. higher energy cubic and quartic terms in the potential energy of the compressed or elongated springs, provides a mechanism for coupling the phonons together. Such higher order terms are generally small but they alone are responsible for such physical properties as thermal expansion, the approach to thermal equilibrium, and thermal conductivity. The influence of the cubic and quartic terms in the potential energy depends on the amplitude of the displacements being almost negligible for small displacements. This basically is why the sound waves produced in the steel bar ring for so long a period of time and travel virtually unattenuated at the speed of sound over the length of the bar. Associated with these sound waves are atomic displacements less than 10^{-8} of the distance between atoms. On the other hand the amplitude of vibration for thermal waves are at least 10^6 orders of magnitude greater so that anharmonicity quickly couples the phonons together. This effectively scatters these waves so that the transfer of heat energy proceeds slowly via a diffusion process.

If our steel rod is replaced by a TiNi alloy called Nitinol and struck at about 100°F a similar metallic "ring" is heard but by lowering the temperature to about 80°F the rod can no longer be caused to "ring". The effect over such a small temperature range is quite dramatic and in fact even at very high stress levels the compressional waves are quickly damped and converted into heat. The prospects of employing this high damping capacity to absorb vibrations in mechanical systems appear promising.

The reason for the very effective damping in NiTi at room temperature is related to the crystallographic (martensitic) phase change that occurs. As a precursor to this transition we find a so-called soft mode building up in the phonon spectrum i.e. certain shear waves develop a very weak spring constant associated with the forces returning them to their equilibrium position after displacement. These correspond to the very directions the atoms will move when they undergo the crystal structure change. At the transition temperature the atomic positions are at the same energy so that even a relatively weak compressional or shear wave can unbalance

this energy difference and cause large displacements of the atoms. When the displacements are large, anharmonicity becomes effective and this in effect enables the long wave length acoustical waves to be quickly damped out and converted into heat. From the point of view of damping materials, the conversion of vibrations into heat is very desirable since the energy of a phonon is proportional to its frequency so that one thermal phonon (10^{13} hertz) can absorb 10^{10} acoustical phonons (10^3 hertz). The conversion of relatively large quantities of vibrational energy produces very small temperature rises.

Any theoretical treatment of anharmonicity and "soft modes" in real crystals is prodigious so we consider it useful to examine a very simple system just to see how anharmonicity couples normal modes together and affects certain physical properties.

The system we have chosen is that of the one-dimensional coupled oscillators each of identical mass M coupled between two rigid (or non-rigid) walls by three identical springs. The potential energy of each spring is represented by a quadratic term (harmonic) and two anharmonic terms, one cubic (stronger in compression) and one quartic so that the total potential energy of the coupled oscillators becomes (rigid walls)

$$V = \tfrac{1}{2} \kappa x_1{}^2 - b^{3/2} x_1{}^3 + g^2 x_1{}^4 + \tfrac{1}{2} \kappa x_2{}^2 \; b^{3/2} x_2{}^3 + g^2 x_2{}^4 + \tfrac{1}{2} \kappa (x_1 - x_2)^2$$

$$+ b^{3/2}(x_1 - x_2)^3 + g^2 (x_1 - x_2)^4 \tag{1}$$

where κ, b and g represent the spring constants respectively of the quadratic, cubic and quartic terms. Since we wish to examine the effect of the anharmonic terms on the normal modes which exist in the absence of the cubic and quartic terms of equation (1) we transform to the system of normal coordiantes ξ and η given by

$$\xi = \tfrac{1}{2}(x_1 + x_2) \left.\vphantom{\begin{matrix}a\\b\end{matrix}}\right\}$$
$$\eta = \tfrac{1}{2}(x_1 - x_2) \tag{2}$$

so that the potential is now

$$V = \kappa(\xi^2 + 3\eta^2) - 6b^{3/2}\eta(\xi^2 - \eta^2) + 2g^2(\xi^2 + 3\eta^2)^2. \tag{3}$$
$$\text{quadratic} \qquad\qquad \text{cubic} \qquad\qquad \text{quartic}$$

The second and third terms on the right-hand side of equation (3) representing the cubic and quartic terms will be considered small relative to the quadratic term so that we can use a perturbation

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treatment.

In the absence of the perturbation, the Schrödinger equation is soluble exactly, leading to a wave function which is a simple product of wave functions, one for each mode,

$$\psi = \psi_m(\xi)\psi_n(\eta)$$

$$\psi_m(\xi) = \left(\frac{a}{2^m m! \sqrt{\pi}}\right)^{1/2} H_m(a\xi) \exp\left(-\tfrac{1}{2} a^2\xi^2\right)$$

$$\psi_n(\eta) = \left(\frac{\sqrt{3}a}{2^n n! \sqrt{\pi}}\right)^{1/2} H_n(3^{1/4}a\eta) \exp\left(-\tfrac{1}{2}\sqrt{3}a^2\eta^2\right) \tag{4}$$

$$a = \left\{\frac{2\pi(M\kappa)^{1/2}}{h}\right\}^{1/2}$$

where $H_m(y)$ is the Hermite polynomial. The eigenvalues of the system are

$$E = (m + \tfrac{1}{2})h\nu + (n + \tfrac{1}{2})\sqrt{3}h\nu$$

$$\nu = \frac{1}{2\pi}\left(\frac{\kappa}{M}\right)^{1/2} \tag{5}$$

harmonic approximation

where the quantum numbers m and n assume integral values including zero, and refer respectively to the ξ and η normal modes. The ξ normal mode represents simple harmonic motion in a system in which the observer is always positioned at one-half the algebraic sum of the the real displacements x_1 and x_2, while the η normal mode is the same for the average of the difference of the displacements. The natural frequency of the η normal mode is $\sqrt{3}$ times the natural frequency ν of the ξ normal mode, equation (5).

When we apply the perturbations of equation (3) we find the cubic term vanishes in first order. We have, therefore, calculated the cubic term to second order and the quartic term to first order. The new set of eigenvalues becomes

$$E \approx (m + \tfrac{1}{2})h\nu + (n + \tfrac{1}{2})\sqrt{3}h\nu - \frac{b^3}{a^6 h\nu}(7\cdot 4m - 3m^2 + 20\cdot 7mn + 3\cdot 2 + 15n^2 + 25\cdot 4n)$$

quadratic term   cubic term

$$+ \frac{g^2}{a^4}(6\cdot 5m + 3m^2 + 6\cdot 9mn + 7\cdot 7 + 9n^2 + 12\cdot 5n). \tag{6}$$

quartic term

New terms now appear in the eigenvalues which are products of the quantum numbers m and n and which are associated respectively with the ξ and η 'normal modes'. Thus one result of anharmonicity is that the excitation of one of the 'normal modes' affects the energy levels of the other. (The words 'normal modes' are now in quotation marks since they strictly refer to the harmonic solutions).

We can select values of b and g to be approximately those obtained from an expansion of the Morse potential since this potential provides a good fit to diatomic molecules

$$V = D \left[\exp \left\{ -2x \left(\frac{\kappa}{2D} \right)^{1/2} \right\} - 2 \exp \left\{ -x \left(\frac{\kappa}{2D} \right)^{1/2} \right\} \right] \qquad (7)$$

Morse potential

where D is the depth of the potential well and κ the spring constant. Expanding around the minimum one obtains

$$V \simeq \frac{1}{2} \left[\kappa x^2 - \frac{\kappa^{3/2} x^3}{(2D)^{1/2}} + \frac{\kappa^2 x^4}{24D} \right]$$

which by a term-by-term comparison with equation (1) gives

$$\left. \begin{array}{l} b^{3/2} = \dfrac{\kappa^{3/2}}{(8D)^{1/2}} \\[2em] g^2 = \dfrac{7\kappa^2}{48D} \end{array} \right\} \qquad (8)$$

so that for $h\nu/D \simeq 10^{-2}$ † equation (6) becomes

$$E \simeq h\nu \left[(m + \tfrac{1}{2}) + \sqrt{3}(n + \tfrac{1}{2}) + 10^{-2}(0 \cdot 02m + 0 \cdot 81m^2 - 1 \cdot 58mn \right.$$

$$\left. + 0 \cdot 69 - 0 \cdot 57n^2 - 0 \cdot 57n) \right] \qquad (9)$$

energy levels for a Morse potential.

† In a typical case $h\nu$ is of order $k\theta$ (where θ is the Debye temperature) and D is of the order of the cohesive energy, so that a value of 10^{-2} for $h\nu/D$ is reasonable.

While the levels of low quantum numbers are only slightly altered, the
higher levels are altered significantly owing to anharmonicity, and
in some cases levels even cross. It is clear from equation (9) that
the energy levels in the anharmonic treatment can not be simply re-
presented by a modified harmonic spectrum, i.e. one in which the two
natural frequencies ν and $\sqrt{3}\nu$ are modified with increasing tempera-
ture so as to preserve the simple form of equation (5). This must
be considered an artifice that avoids the basic aspect of anharmon-
icity (i.e. a change in the spectrum of eigenvalues).

We may now employ thermodynamics to evaluate the high
temperature specific heat for the coupled oscillators, equation
(6). Setting

$$b^3/a^6(h\nu)^2 = c \ll 1 \qquad \text{(cubic)}$$

$$g^2/a^4(h\nu) = q \ll 1 \qquad \text{(quartic)} \tag{10}$$

and recalling that

$$\sum_0^\infty m^2 e^{-mx} = e^{-x}\frac{1 + e^{-x}}{(1 - e^{-x})^3}$$

we obtain the partition function f at high temperatures, i.e.
$kT \gg h\nu$ (neglecting zero point terms which do not contribute to
the specific heat):

$$f = \frac{1}{\sqrt{3}\chi^2}\left[1 + 22c - 13\cdot7q + \frac{14c}{\chi} - \frac{10q}{\chi}\right] \tag{11}$$

$$\chi = h\nu/kT$$

so that the specific heat becomes at constant length

$$C_L = kT\frac{\partial^2}{\partial T^2}(T \ln f) \approx 2k\left\{1 + (14c - 10q)\frac{kT}{h\nu}\right\}. \tag{12}$$

Thus in agreement with the classical treatment the leading term in
the departure of the specific heat from the Dulong-Petit value
of 2k is linear in T either positive or negative depending on the
magnitude of the cubic and quartic terms in the potential. For
a Morse type potential ($c/q = 6/7$) the term is positive.

If we allow the walls to move so that the length of each
spring is charged by δ (δ positive for compression), new terms appear

in the potential which are added to those in equation (3). The
leading new terms are

$$\tfrac{3}{2} \kappa \delta^2 + (6 \delta b^{3/2} + 12 g^2 \delta^2)(\xi^2 + 3\eta^2) \qquad (13)$$

so that by replacing $\kappa \rightarrow \kappa + 6 \delta b^{3/2} + 12 g^2 \delta^2$ for the ξ and η modes and
adding $\tfrac{3}{2} \kappa \delta^2$ to equation (6) we have the new set of eigenvalues as a
function of δ. If we evaluate the high temperature free energy for
this set of eigenvalues and minimize the free energy relative to δ,
we obtain in the high temperature region

$$\delta \simeq - \frac{2b^{3/2}kT}{\kappa^2} \qquad (14)$$

showing that the system expands with temperature. The two frequencies
of the system ν and $\sqrt{3}\nu$ are now temperature dependent and become

$$
\begin{aligned}
\nu \rightarrow \nu \left(1 - \frac{6b^{3/2}kT}{\kappa^2}\right) & \qquad \xi \text{ mode} \\[2mm]
\sqrt{3}\nu \rightarrow \sqrt{3}\nu \left(1 - \frac{6b^{3/2}kT}{\kappa^2}\right) & \qquad \eta \text{ mode}
\end{aligned}
\Biggr\} . \qquad (15)
$$

For a soft mode to be effective the cubic and quartic terms
must become proportionately greater than the quadratic term.