

THERMODYNAMICS OF HARMONIC OSCILLATORS - CLASSICAL AND QUANTUM

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Shankar, R. (1994), *Principles of Quantum Mechanics*, Plenum Press.
Section 7.5, Exercise 7.5.4.

One application of harmonic oscillator theory is in the behaviour of crystals as a function of temperature. A reasonable model of a crystal is of a number of atoms that vibrate as harmonic oscillators. From statistical mechanics, the probability $P(i)$ of finding a system in a state i is given by the Boltzmann formula

$$(1) \quad P(i) = \frac{e^{-\beta E(i)}}{Z}$$

where $\beta = 1/kT$, with k being Boltzmann's constant and T the absolute temperature, and Z is the partition function

$$(2) \quad Z = \sum_i e^{-\beta E(i)}$$

The thermal average energy of the system is then

$$(3) \quad \bar{E} = \sum_i E(i) P(i)$$

$$(4) \quad = \frac{\sum_i E(i) e^{-\beta E(i)}}{Z}$$

$$(5) \quad = -\frac{\partial (\ln Z)}{\partial \beta}$$

For a classical harmonic oscillator, the energy is a continuous function of the position x and momentum p :

$$(6) \quad E_{cl} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

The classical partition function is then

$$(7) \quad Z_{cl} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\beta p^2/2m} e^{-\beta m\omega^2 x^2/2} dp dx$$

$$(8) \quad = \int_{-\infty}^{\infty} e^{-\beta p^2/2m} dp \int_{-\infty}^{\infty} e^{-\beta m\omega^2 x^2/2} dx$$

$$(9) \quad = \sqrt{\frac{2\pi m}{\beta}} \sqrt{\frac{2\pi}{\beta m\omega^2}}$$

$$(10) \quad = \frac{2\pi}{\omega\beta}$$

Where we used the standard formula for Gaussian integrals to get the third line. The average classical energy is, from 5

$$(11) \quad \bar{E}_{cl} = -\frac{\partial (\ln Z_{cl})}{\partial \beta} = \frac{1}{\beta} = kT$$

The average energy of a classical oscillator thus depends only on the temperature, and not on the frequency ω .

For a quantum oscillator, the energies are quantized with values of

$$(12) \quad E(n) = \hbar\omega \left(n + \frac{1}{2} \right)$$

The quantum partition function is therefore

$$(13) \quad Z_{qu} = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}$$

The sum is a geometric series, so we can use the standard result for $|x| < 1$:

$$(14) \quad \sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

This gives

$$(15) \quad Z_{qu} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

The mean quantum energy is again found from 5, although this time the derivative is a bit messier, so is most easily done using Maple. However, by hand, you'd get

$$(16) \quad \bar{E}_{qu} = -\frac{\partial (\ln Z_{qu})}{\partial \beta}$$

$$(17) \quad = \frac{1 - e^{-\beta \hbar \omega}}{e^{-\beta \hbar \omega/2}} \left[-\frac{1}{2} \frac{\hbar \omega e^{-\beta \hbar \omega/2}}{1 - e^{-\beta \hbar \omega}} - \frac{\hbar \omega e^{-\beta \hbar \omega/2} e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2} \right]$$

$$(18) \quad = \frac{\hbar \omega}{2} \left(\frac{1 + e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \right)$$

$$(19) \quad = \frac{\hbar \omega}{2} \left(\frac{1 - e^{-\beta \hbar \omega} + 2e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \right)$$

$$(20) \quad = \hbar \omega \left(\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega} - 1} \right)$$

The average energy is the ground state energy $\hbar \omega/2$ plus a quantity that increases with increasing temperature (decreasing β). For small β we have

$$(21) \quad \bar{E}_{qu} \rightarrow \hbar \omega \left(\frac{1}{2} + \frac{1}{1 + \beta \hbar \omega - 1} \right)$$

$$(22) \quad = \frac{\hbar \omega}{2} + \frac{1}{\beta}$$

$$(23) \quad \rightarrow kT$$

since as $\beta \rightarrow 0$, $\frac{1}{\beta} \gg \frac{\hbar \omega}{2}$. Thus the quantum energy reduces to the classical energy 11 for high temperatures. The 'high temperature' condition is that

$$(24) \quad \frac{1}{\beta} \gg \frac{\hbar \omega}{2}$$

$$(25) \quad T \gg \frac{\hbar \omega}{2k}$$

So far, we've considered the average behaviour of only one oscillator. Suppose we now have a 3-d crystal with N_0 atoms. Assuming small oscillations we can approximate its behaviour by a system of $3N_0$ decoupled oscillators. In the classical case, the average energy is found from 11:

$$(26) \quad \bar{E}_{cl} = 3N_0 \bar{E}_{cl} = 3N_0 kT$$

The heat capacity per atom is the amount of heat (energy) ΔE required to raise the temperature by ΔT , so

$$(27) \quad C_{cl} = \frac{1}{N_0} \frac{\partial \bar{\mathcal{E}}_{cl}}{\partial T} = 3k$$

For the quantum system, we have from 20

$$(28) \quad \bar{\mathcal{E}}_{qu} = 3N_0 \bar{E}_{qu}$$

$$(29) \quad = 3N_0 \hbar \omega \left(\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega} - 1} \right)$$

The quantum heat capacity is therefore

$$(30) \quad C_{qu} = \frac{1}{N_0} \frac{\partial \bar{\mathcal{E}}_{qu}}{\partial T}$$

$$(31) \quad = 3\hbar \omega \frac{\partial}{\partial \beta} \left(\frac{1}{e^{\beta \hbar \omega} - 1} \right) \frac{d\beta}{dT}$$

$$(32) \quad = 3 \frac{\hbar^2 \omega^2}{kT^2} \frac{e^{\hbar \omega / kT}}{(e^{\beta \hbar \omega} - 1)^2}$$

We can define the *Einstein temperature* as

$$(33) \quad \theta_E \equiv \frac{\hbar \omega}{k}$$

which gives the heat capacity as

$$(34) \quad C_{qu} = 3k \frac{\theta_E^2}{T^2} \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

For large temperatures, the exponent θ_E/T becomes small, so we have

$$(35) \quad C_{qu} \xrightarrow{T \gg \theta_E} 3k \frac{\theta_E^2}{T^2} \frac{1 + \theta_E/T}{(1 + \theta_E/T - 1)^2}$$

$$(36) \quad \rightarrow 3k$$

For low temperatures $e^{\theta_E/T} \gg 1$ so we have

$$(37) \quad C_{qu} \xrightarrow{T \ll \theta_E} 3k \frac{\theta_E^2}{T^2} \frac{e^{\theta_E/T}}{e^{2\theta_E/T}}$$

$$(38) \quad = 3k \frac{\theta_E^2}{T^2} e^{-\theta_E/T}$$

The heat capacity again reduces to the classical value for high temperatures. The observed behaviour at low temperatures is that $C_{qu} \rightarrow T^3$, so this simple model fails for very low temperatures. However, as is shown by Shankar's figure 7.3 Einstein's quantum model is actually quite good for all but the lowest temperatures.