

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

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

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

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

The thermal average energy of the system is then

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

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

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

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

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

The classical partition function is then

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

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

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

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

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

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

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

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

The quantum partition function is therefore

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

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

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

This gives

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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:

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

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

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

For the quantum system, we have from 20

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

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

The quantum heat capacity is therefore

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

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

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

We can define the *Einstein temperature* as

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

which gives the heat capacity as

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

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

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

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

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

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

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

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.