

Dulong-Petit's Law

Main idea

In all the theories, the starting point is that the vibrational energy of a crystal (or substance in any form) containing N atoms is equal to the energy of $3N$ harmonic oscillators (harmonicity or anharmonicity of oscillators will be discussed later, but for this study, they can be taken as harmonic). In a three-dimensional (3D) crystal, each atom has three degrees of freedom, so N atoms in the crystal has $3N$ degrees of freedom and hence $3N$ oscillators. If we could know the frequency and energy ($h\nu = \text{energy}$) of each and every $3N$ oscillators at a certain temperature T , and also the frequency and energy of these $3N$ oscillators at temperature $(T + 1)$, the difference in energy at these two temperatures would have given us the exact value of specific heat. However, in any crystal, $3N$ is a very large number, and we do not have any means to see or estimate the frequency of each and every oscillator. In such a case, one resorts to making models that mimic the physical situation as closely as possible and convert the problem into mathematical language and then find a mathematical solution. Ultimately, it has to be tested by comparison with the experimental result. Each step in formulating a working model and inventing mathematics to get a solution of the problem, which looks reasonable with some degree of agreement with the experimental result, is quite difficult and requires intuition and deep insight into the problem. In a model, if there is semblance of agreement with the experimental result, people try to improve this model or propose a new model to achieve the closest agreement with the experiment.

Assumptions

In Dulong and Petit's model, they assumed that each oscillator in the crystal vibrates with a certain frequency (natural frequency, say ω_0), but they may have different energies, because the amplitude of oscillation may be different for different atoms. One thing that has to be mentioned is that the Dulong–Petit law came much before quantum mechanics was discovered. The method of Dulong–Petit was to find the average energy \bar{E} associated with an oscillator and then for finding the total energy of the crystal, multiply the average energy \bar{E} by $3N$. Each oscillator was supposed to have a kinetic energy of $p^2/2m$ and a potential energy of $\frac{1}{2} \cdot m\omega_0^2 x^2$, where p is the momentum, m the mass of an atom, and x the displacement from the equilibrium position.

Mathematical treatment

Hence, the total energy of vibration is given as

$$E = \frac{p^2}{2m} + \frac{1}{2} \cdot m\omega_0^2 x^2.$$

From Equation (5.2), one has to find the average energy \bar{E} of the oscillator assuming Boltzmann distribution in the energy of oscillators. Hence,

$$\bar{E} = \frac{\int E \exp\left(\frac{-E}{KT}\right) dE}{\int \exp\left(\frac{-E}{KT}\right) dE}$$

$$= \frac{\iint \left(\frac{p^2}{2m} + \frac{1}{2} m\omega_0^2 x^2 \right) \exp - \left(\frac{p^2}{2mKT} + \frac{1}{2} \frac{m\omega_0^2 x^2}{KT} \right) dp dx}{\iint \exp - \left(\frac{p^2}{2mKT} + \frac{1}{2} \frac{m\omega_0^2 x^2}{KT} \right) dp dx}$$

$$\iint \left(\frac{p^2}{2m} \right) \exp\left(\frac{-p^2}{2mKT}\right) \exp\left(\frac{-m\omega_0^2 x^2}{2KT}\right) dp dx \quad \iint \left(\frac{1}{2} \right) m\omega_0^2 x^2 \left(\exp\left(\frac{-p^2}{2mKT}\right) \right) \exp\left(\frac{-m\omega_0^2 x^2}{2KT}\right) dp dx$$

$$= \frac{\iint \left(\frac{p^2}{2m} \right) \exp\left(\frac{-p^2}{2mKT} \right) \exp\left(\frac{-m\omega_0^2 x^2}{2KT} \right) dp dx}{\iint \exp\left(\frac{-p^2}{2mKT} \right) \exp\left(\frac{-m\omega_0^2 x^2}{2KT} \right) dp dx} + \frac{\iint \left(\frac{1}{2} \right) m\omega_0^2 x^2 \left(\exp\left(\frac{-p^2}{2mKT} \right) \right) \exp\left(\frac{-m\omega_0^2 x^2}{2KT} \right) dp dx}{\iint \left(\exp\left(\frac{-p^2}{2mKT} \right) \exp\left(\frac{-m\omega_0^2 x^2}{2KT} \right) \right) dp dx}$$

$$= \frac{\int_p \left(\frac{p^2}{2m} \right) \exp\left(\frac{-p^2}{2mKT} \right) dp}{\int_p \exp\left(\frac{-p^2}{2mKT} \right) dp} + \frac{\int_x \frac{1}{2} \cdot m\omega_0^2 x^2 \exp\left(\frac{-m\omega_0^2 x^2}{2KT} \right) dx}{\int_x \exp\left(\frac{-m\omega_0^2 x^2}{2KT} \right) dx}.$$

The integrals in Equation _{above} can be solved using the following integrals:

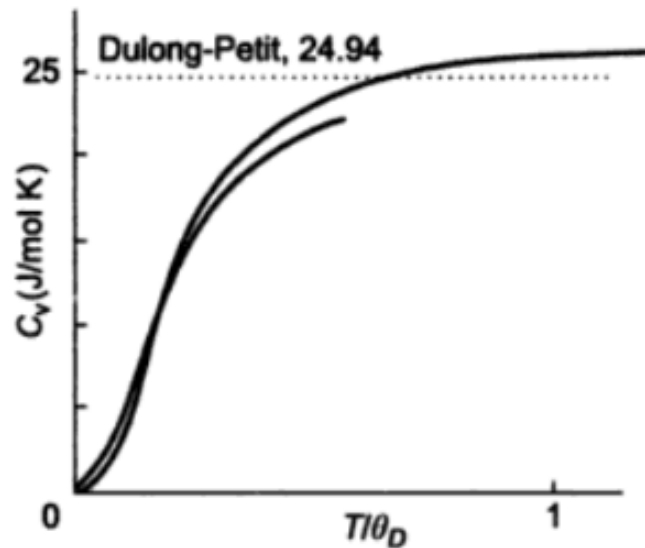
$$\int_0^{\infty} u^2 \exp(-au^2) du = \frac{1}{4} \sqrt{\frac{\pi}{a^3}} \quad \text{and}$$

$$\int_0^{\infty} \exp(-au^2) du = \frac{1}{2} \sqrt{\frac{\pi}{a}}.$$

Taking the help of standard integrals given above, by putting $p^2 = u^2$ and $a = \frac{1}{2mKT}$ and similar terms, both the first and second terms = $\frac{1}{2} KT$. So

$$\bar{E} \text{ in the equation (5.3)} = KT.$$

$\frac{1}{2} KT$ lower from kinetic energy and other $\frac{1}{2} KT$ from potential energy



Thus, the total vibrational energy of the crystal is equal to $3NKT$ and

$$C_{\theta} = 3NK = 3R,$$

where R is the gas constant, $\approx 1.97 \text{ Cal mol}^{-1} \text{ K}^{-1}$.

Thus,

$$C_{\theta} = 5.96 \text{ Cal mol}^{-1} \text{ K}^{-1}.$$

This is an important result that says that the gram-molecular specific heat of any substance is a constant and is equal to $5.96 \text{ Cal mol}^{-1} \text{ K}^{-1}$. This is known as the Dulong-Petit law and was verified for many substances. However, this law holds good only at high temperatures as shown in Figure^{above}. At low temperatures, specific heat is quite small and increases quite rapidly with the increase in temperature until a temperature is reached beyond which the specific heat becomes constant or strictly follows the Dulong-Petit's law (see Figure^{above}). However, this classical theory of specific heat does not say anything about the temperature variation of specific heat. Recognizing this anomaly, Einstein proposed another theory of specific heat purportedly to explain the temperature dependence of specific heat.